MONOGRAPHS ON PHYSICS

EDITED BY

SIR J. J. THOMSON, O.M., F.R.S.

CAVENDISH PROFESSOR OF EXPERIMENTAL PHYSICS, CAMBRIDGE

AND

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PROFESSOR OF PHYSICS IN THE UNIVERSITY OF LONDON

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THE PHYSICAL PROPERTIES

OF

COLLOIDAL SOLUTIONS

BY

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PREFACE.

THE present attempt to give an outline of the study of colloidal solutions has to do particularly with its interest to the student of Physics. Both by aim and necessity the writer has kept in mind the relation of colloids to the development of Physics. For this reason rather extended treatment is given of the development of the ultramicroscope and the confirmation of the kinetic theory of matter afforded by the theoretical and experimental study of the Brownian movement. When we come to deal with the phenomena of the charge possessed by the colloidal particle, the surface tension between the particle and the surrounding medium, and the mechanism of coagulation, we approach the most important problem of physics and chemistry, namely, the unfolding of the interaction of the ultimate particles of matter on one another.

The plan of the book is apparent from the table of contents. Under the head of preparation and classification, I have attempted to offer systematic tables of various classes of colloids having something in common, and have quoted types of methods of preparation to enable the reader to find out where to look for detailed information. Chapters III. to VII. inclusive might be called the physics of colloidal study; they embrace the greater part of the book and will probably appeal particularly to the student of pure physics. In dealing with the question of the coagulation of sols, we come to the part of the subject on which probably the greatest amount of work has been done and from which we may expect most definite ideas as to the reason for the stability of colloidal solutions.

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As to the arrangement of the bibliography, the numbers in each chapter refer to the list immediately following the chapter. Although this entails a few repetitions, it is hoped that it will prove of more immediate value to the reader than a general bibliography for the whole at the end of the volume. In addition to the references throughout the book, the following treatises should be listed as standards of reference in colloidal study:—

Zsigmondy, "Zur Erkenntnis der Kolloide". 1905. (English translation by Alexander. 1909.)
Cotton et Mouton, "Les ultramicroscopes et les objets ultramicroscopiques". 1906.
Arthur Müller, "Allgemeine Chemie der Kolloide". 1907.
Wo. Ostwald, "Grundriss der Kolloidchemie". 1909.
The. Svedberg, "Herstellung Kolloider Lösungen". 1909.
Freundlich, "Kapillarchemie". 1909.
van Bemmelen, "Die Absorption". 1911.
Zsigmondy, "Kolloidchemie". 1912.
The. Svedberg, "Die Existenz der Moleküle". 1912.

Side by side with these, one must mention the "Zeitschrift für Chemie und Industrie der Kolloide (Kolloid-Zeitschrift)" and the "Kolloidchemische Beihefte," published by Wo. Ostwald; anyone hoping to have any complete conception of the subject should be familiar with these journals from their beginnings. The few references made to these journals in the bibliographies do not represent adequately one's real indebtedness to them.

I desire to express here the sense of gratitude I feel to Sir J. J. Thomson, who first suggested the subject of colloids to me, and who has invariably shown a keen and sympathetic interest in the work, and also to Mr. W. B. Hardy, F.R.S., one of the pioneers of the modern work on colloids who, during the writer's residence in Cambridge, was a continual source of help and inspiration.

E. F. BURTON.

UNIVERSITY OF TORONTO,
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CHAPTER I.

INTRODUCTION.

RECENT advances in many branches of scientific research have tended to emphasize the essential unity of all the sciences in the struggle to unfold the mysteries of the phenomena of life and nature. Biology, physiology, biochemistry, physical chemistry, and pure physics deal fundamentally with the same laws, and it is becoming more and more difficult to delimit the region peculiar to each. Few lines of recent research exhibit such ramifications of interest as that dealing with colloidal solutions.

Generally, a colloidal solution may be defined as a suspension, in a liquid medium, of fine particles which may be graded down from those of microscopic to those of molecular dimensions; these particles may be either homogeneous matter, solid or liquid, or solutions of a small percentage of the medium in an otherwise homogeneous complex. Such solutions may be prepared in almost numberless ways,[1] and, in their properties, may betray variations as numerous as the methods of preparation. The one property common to all such solutions is that the suspended matter will remain almost indefinitely in suspension in the liquid, generally in spite of rather wide variations in temperature and pressure; the natural tendency to settle due to the attraction of gravitation is overbalanced by some other force tending to keep the small masses in suspension.

The rapid development in our knowledge of these solutions is due to the confluence of some three or four lines of investigation, each having its beginning early in the last century.

1. For several hundred years biologists have observed and studied the motions of microscopic animalcules in liquids.

About the year 1827, Robert Brown,[2] the English biologist, found that even inanimate fine particles in liquids possessed a similar characteristic motion—a continual zig-zag movement which has come to be called the Brownian movement. This curious motion has been studied continuously since Brown's time, and has recently contributed important quantitative confirmation of the kinetic theory of matter.[3]

2. One of Faraday's keen ambitions was to show experimentally the connexion between electricity and light. In pursuance of this object, he at one time sought to find the effect exerted on light by very fine particles of metals suspended in liquid or solid media, e.g. in water or glass.[4] Faraday prepared several aqueous (colloidal) solutions of gold, and first suggested what is now believed to be the true constitution of these solutions. A few years later Tyndall[5] developed the experiment by which such small particles may be revealed by the lateral diffusion of a beam of light traversing the solution. This led to the theoretical work on the blue colour of the sky and, later, to the investigation of the optical absorption of colloidal solutions.

3. About 1850, English microscopists, in their endeavour to increase the magnifying power of the microscope, introduced the method of illumination known under the name of dark background illumination.[6] The characteristic of this method is that the direct illuminating beam is screened off, and the object is made visible by the light which it diffuses up the tube of the microscope. These early investigators used this method for the lateral illumination of ordinary microscopic objects, e.g. diatoms; however, after the invention of the slit ultramicroscope by Zsigmondy and Siedentopf,[7] the early method of dark ground illumination was revived in the forms of other recent ultramicroscopes.

4. The most direct antecedent of the modern work on colloidal solutions is found in the investigations of Graham[8] on the rates of diffusion of various substances in water. He found that all substances fall into two classes—those with very slow diffusion (which he called colloids), and those with a higher order of diffusion rate (crystalloids). Using permeable septa,

such as employed by early workers on osmosis, he found that his colloids did not diffuse through them at all, while the crystalloidal materials went through the septa quite readily.

On account of these diffusion experiments, Graham suggested that the "colloidal molecules may be constituted by the grouping together of a number of smaller crystalloidal molecules". This being the case, they should show the Tyndall phenomenon. Following out Graham's ideas, Linder and Picton[9] prepared a series of solutions of arsenious sulphide, in which they were able to grade the sizes of the particles from aggregates visible in the ordinary microscope to those just bordering on the upper limit of the size of molecules. Many continental workers were also engaged in the examination of similar solutions; in particular, Zsigmondy and Siedentopf set themselves to apply the principle of the Tyndall phenomenon to the ordinary microscope; the result was the first ultramicroscope. Soon there followed from various optical manufacturers the simpler types of ultramicroscopes which adopted, consciously or unconsciously, the method of dark ground illumination of the early English microscopists.

The ultramicroscope, when used to view colloidal solutions, showed that the latter possessed a very noticeable Brownian movement, much more brilliant than ordinary microscopic particles since the rate of motion increases rapidly as the size of the particles decreases.

The invention of the ultramicroscope marked the beginning of the modern widespread study of colloidal solutions. It afforded experimental evidence necessary to generalize the results of the many lines of research indicated above.

The chapters which follow will deal with the physical aspect of colloidal solutions from four points of view: (1) their preparation and classification; (2) the general properties of such solutions; (3) the theoretical importance of the study of such solutions, and (4) the practical importance of colloids, as for example in physiology and technology.

In addition to the properties of colloidal solutions already indicated, viz., their stability of state and the Brownian movement of the particles, they have very important electrical properties. In common with coarser suspensions of such materials as sand, graphite, quartz, amber, etc., in various fluids, generally speaking, these colloidal particles are found to be set in motion when a potential difference is applied between two electrodes placed in the solution—i.e. they move in an electric field and are therefore said to be electrically charged. In some cases the particles are positively charged, in others negatively. Again, although these solutions are very stable and when left undisturbed will remain practically unchanged, the suspended matter may be precipitated in a variety of ways; as a general rule, the addition to the solution of electrically conducting solutions (electrolytes) will induce coagulation in a short time.

The theoretical importance of colloidal solutions is widespread; to the physicist, probably their chief interest may be summed up under three heads. In the first place, the work of Einstein,[10] Smoluchowski,[11] and Langevin,[12] in offering exact mathematical formulæ whereby the Brownian movement may be quantitatively tested, and the investigations of Perrin [13] on the distribution of the particles throughout the volume of a liquid, afford most striking evidence of the truth of the fundamental hypotheses of the kinetic theory of liquids and gases, and of the existence of the molecule. Secondly, Faraday's work on the optical effects of such solutions has been recently supplemented by many researches which have attempted to solve the riddle of the form and structure of the particles.[14] Thirdly, the perennial question as to the reason for the stability of these solutions remains. The various physical forces which may be involved—electrical attractions or repulsions, surface tension, molecular shocks—suggest a puzzle, the solution of which will undoubtedly give us most valuable information regarding the forms of energy involved in the liquid and solid states.

Judging by the literature on the subject and considering the structure and action of the constituent parts of the animal body, we may conclude that the study of colloidal solutions is of surpassing interest to the zoologist and physiologist. The invention of the ultramicroscope has brought into view bodies, e.g. certain germs, which were theretofore undiscovered. The abundance and ubiquity of natural colloids in the human body brings into prominence the work on semi-permeable membranes, surface tension, and the rôle played by the *Schutzkolloid* (see p. 17). Indeed, Perrin[15] has suggested a colloidal explanation of the process of primary cell growth and cell division, an idea which is somewhat supported by the phenomenon of galvanotropism of microscopic animals.[16, 17]

A mere enumeration of the use of colloids in technology would occupy too much space at this point.[18] Dyeing, tanning, glass manufacture, cement hardening, afford examples of the way in which the properties of these solutions were made use of before their real constitution had become a subject of theoretically important work. In reality there are very few modern manufacturing processes which do not employ such solutions. Equally important is the rôle of such solutions in the processes of nature; as an instance of this, according to van Bemmelen,[19] the retentive power of rich soils for the salts necessary to the growth of plants is due directly to the existence of colloidal solutions in the humus and clay of the soil.

Although there is, as yet, little finality in the study of these solutions, the vast amount of work that has been and is being done will probably justify this attempt to outline the present state of our knowledge of them.

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CHAPTER II.

PREPARATION AND CLASSIFICATION OF COLLOIDAL SOLUTIONS.

THE term, colloid, was used first by Graham, about 1861, to denote a class of substances, many of them of a gummy consistency, which had an extremely low rate of diffusion through media in which they were dissolved. As the result of an extensive series of experiments on the rates of diffusion of various compounds, he was led to divide all substances into two classes, the rate of diffusion of materials in one of the groups being much larger than the rate of those belonging to the other group. He found that such substances as silicic acid, soluble alumina, and certain organic compounds, viz., gum-arabic, tannin, dextrin, caramel, and albumen, possess extremely slow rates of diffusion into pure water, compared with the rates of such compounds as sodium chloride, hydrochloric acid, etc. The former group he called colloids, while the latter he designated crystalloids on account of the fact that they crystallize from saturated solutions. Further examination of the properties of the substances in the two classes showed him that there was a very general line of cleavage between the two groups.

"They appear like different worlds of matter, and give occasion to a corresponding division of chemical science. The distinction between these kinds of matter is that subsisting between the material of a mineral and that of an organized mass.

"The colloidal character is not obliterated by liquefaction, and is, therefore, more than a modification of the physical condition of solid. Some colloids are soluble in water, as gelatine and gum-arabic; and some are insoluble, like gum-tragacanth. Some colloids again form solid compounds with water, as gelatine and gum-tragacanth, while others like tannin do not. In such points the colloids exhibit as great a diversity of property as the crystalloids. A certain parallelism is maintained between the two classes notwithstanding their differences.

"The phenomena of the solution of a salt or crystalloid probably all appear in the solution of a colloid, but greatly reduced in degree. The process becomes slow; time, indeed, appearing essential to all colloidal changes. The change of temperature usually occurring in the act of solution becomes barely perceptible. The liquid is always sensibly gummy or viscous when concentrated. The colloid, although often dissolved in a large proportion by its solvent, is held in solution by a singularly feeble force. Hence colloids are generally displaced or precipitated by the addition to their solution of any substance from the other class. Of all the properties of liquid colloids, their slow diffusion in water, and their arrest by colloidal septa are the most serviceable in distinguishing them from crystalloids. Colloids have feeble chemical reactions, but they exhibit at the same time a very general sensibility to liquid reagents. . . .

"The inquiry suggests itself whether the colloidal molecule may not be constituted by the grouping together of a number of smaller crystalloidal molecules, and whether the basis of colloidality may not really be this composite character of the molecule."[1]

As indicated above, Graham found that the solution of a colloid would not pass through a membrane of a solid colloid, while solutions of crystalloids do so with the utmost ease. This property is of the greatest importance as a practical means of freeing solutions of colloids from crystalloidal impurities, i.e. by so-called dialysis.

While Graham called the particular substances—gelatine, gum-arabic, etc.—colloids, there is distinct indication in the above quotation that he was well aware of the intimate relation that must subsist between the solvent and the solute. Modern work has shown that it is incorrect to speak of colloidal substances as a particular class. Krafft[2] has observed that the alkali salts of the higher fatty acids—stearate, palmitate, oleate—dissolve in alcohol as crystalloids with normal molecular weights, but in water they are true colloids. The reverse is true of sodium chloride; Paal[3] found that the latter gave a colloidal solution in benzol, while, of course, it gives a crystalloidal solution in water. More recently, Von Weimarn[4] has demonstrated, by the preparation of colloidal solutions of over two hundred chemical substances (salts, elements, etc.), that, by proper manipulation, almost any substance which exists in the solid state can be produced either as a colloid or as a crystalloid; and that in some cases, as shown by many other workers, it is merely a matter of the concentration of the reacting components whether one gets crystalloidal or colloidal solutions.

Consequently, we now speak of matter being in the colloidal state rather than of certain substances as colloids—the essential characteristic of the colloidal state being that the substance will exist indefinitely as a suspension of solid (or, sometimes, probably liquid) masses of very small size in some liquid media, e.g. water, alcohol, benzol, glycerine, etc. According to the medium employed, the resulting solutions or suspensions are called, after Graham, hydrosols, alcosols, benzosols, glycerosols, etc.

When a general treatment of the theory of such solutions is attempted, it is seen that they are related in their properties, on the one hand, to distributions, in finely divided state, of a solid through a solid medium, as for example, gold ruby glass; and, on the other hand, to distributions of finely divided solids in gaseous media as, for example, smoke in air. To all such heterogeneous mixtures of solid, liquid, or gas, in state of suspension in solid, liquid or gaseous media, the name dispersoid has been given; the theory of the equilibrium of dispersoids in general has been treated by Freundlich,[5] Wo. Ostwald,[6] and Von Weimarn.[4] Following the nomenclature adopted by these writers, we shall call the finely divided masses, the disperse phase, while the medium through which the particles are distributed will be called the dispersion medium.

Taking the three states of matter—solid, liquid, and gaseous—we should have the nine different kinds of dispersoids indicated in the following table (Table I), in which is also given examples of the various systems.

TABLE I.

	Disperse phase.	Dispersion medium.	Examples.
1	Solid in	Solid.	Solid solutions, gold ruby glass, carbon in steel, rock salt with sodium.
2	Liquid in	Solid.	Liquid in minerals, water of crystallization.
3	Gas in	Solid.	Gases in minerals, meerschaum, hydrogen in various metals.
4	Solid in	Liquid.	Colloidal solutions of metals.
5	Liquid in	Liquid.	Emulsions of oil in water.
6	Gas in	Liquid.	Air in water, foam.
7	Solid in	Gas.	Smoke in air, salammoniac powder in air.
8	Liquid in	Gas.	Clouds, gases at their critical state.
9	Gas in	Gas.	Not a dispersoid, merely a mixture of molecules.

So-called colloidal solutions are included under groups (4) and (5), chiefly the former. They include such of those dispersoids as have the individuals of the disperse phase with diameters lying between two fairly definite limits. The upper limit is set by those particles which settle under gravitation in a short time; the lower limit is fixed by the power of the ultramicroscope to render the particles visible. So we have, after W. Ostwald, the following classification of these dispersoids :—

Dispersoids. [4] and [5].

	Coarse suspensions.	Colloidal solutions.	Molecular solutions.
Diameters of particles :	$> 0{\cdot}1\ \mu$ *	between $0{\cdot}1\ \mu$ and $1{\cdot}0\ \mu\mu$	$< 1{\cdot}0\ \mu\mu$

* μ equals 10^{-3} mm. = 10^{-4} cm. $\mu\mu$ = 10^{-6} mm. = 10^{-7} cm.

Even among this limited number of dispersoids, we find great diversity of structure and property; in order to recognize the common bonds involved, one needs to evolve some kind of classification of the various solutions. The present state of our knowledge does not justify any very final, far-reaching classification, such as into groups, families, etc. ; but nevertheless the dispersoids do fall into two fairly well-recognized groups,—a division indicated by Graham himself. He notes that the comparatively small number of solutions with which he worked fell into two classes. "Some colloids, as gelatine, gum-tragacanth, form solid compounds with water, while others like tannin do not."[1] These two classes have been differentiated by Noyes[7] as follows: (1) viscous, gelatinizing colloidal mixtures, not (easily) coagulated by salts, and (2) non-viscous, non-gelatinizing, but readily coagulable mixtures. This same division has been retained almost exactly by various writers under different group names, as shown in Table II. Those of the gelatine type may be dissolved directly in the medium; when placed in the dry state in the liquid (usually water) they absorb a large amount of the liquid, gradually swell with the absorption, until, at sufficient dilution, the solid becomes distributed in a finely divided state throughout the medium. According to some workers, we have in these cases a mixture of two solutions, the disperse phase consisting of a solution of water in the fine solid particles, the dispersion medium being a dilute true solution of the solid in the liquid medium. In those of the second group, the solid particles are not so intimately related to the liquid medium, and usually the colloidal state must be brought about by means other than simple direct solution. These various differences between the colloids of the two groups account for the variety of the names assigned by different authors. On the whole, emulsoid and suspensoid seem to be the most suitable, for reasons which will develop in the course of this chapter.

TABLE II.

Author.	Gelatinizing type.	Non-gelatinizing type.
Hardy[8]	Reversible.	Non-reversible.
Billiter[9]	Hydrophilous.	Anhydrophilous.
Henri[10]	Stable.	Unstable.
Noyes[7] Höber[11]	Colloidal solutions.	Colloidal suspensions.
Freundlich[5] Neumann[12]	Lyophile.	Lyophobe.
Bary[13]	Dissolving colloids.	Electrical colloids.
Von Weimarn[4] Wo. Ostwald[6]	Emulsoid.	Suspensoid.

In addition to the peculiarities already noted, the solutions of the gelatinous class, which we shall call emulsoids, have their particles very feebly charged, and do not seem to depend for their stability on the value of this charge. Their very general non-sensitiveness to the addition of traces of electrolytes is another common property linking all such solutions in one class. However, when we consider the sub-class suspensoids, we find a much greater variety of behaviour and have reasons for further classification.

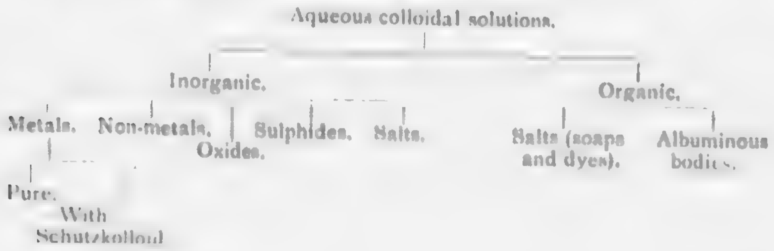
Many methods of classification, depending on the point of view taken, have been suggested: (1) According to the sizes of the particles of the disperse phase; (2) According to the chemical constitution of the disperse phase, i.e. whether element, or salt, etc. (Zsigmondy[14]); (3) According to methods of preparation (Svedberg,[15] Ostwald[6]); (4) According to physical properties and behaviour as colloids, a classification which we shall attempt particularly from the point of view of the physical aspect of these solutions.

1. CLASSIFICATION ACCORDING TO SIZE OF PARTICLES.

The first classification is rather meaningless because the same solution may have particles of various sizes existing in it at one and the same time, and, certainly, such experiments as those of Linder and Picton[16] on arsenic sulphide have shown that solutions of identically the same chemical constitution can be produced with the disperse phase varying in size from that of gross suspensions to that of molecular solutions.

2. CLASSIFICATION ACCORDING TO CHEMICAL CONSTITUTION.

Zsigmondy's classification is particularly useful in reducing the whole range of colloidal solutions to a chemical system. His classification is as follows:—



3. CLASSIFICATION ACCORDING TO METHODS OF PREPARATION.

Comparing the methods of preparation given by various workers (see Svedberg,[15] Müller,[17] Ostwald,[6] Von Weimarn [4]) we have light shed on the diverse properties of colloidal solutions of this class. As pointed out by Svedberg, all the means of preparation of these solutions follow one or other of two general methods. Either the solid is taken *en masse* and in some way dispersed throughout the liquid medium (the so-called dispersion method), or the disperse particles are made synthetically from molecules (the so-called condensation method). In Table III these methods are classified and the aqueous colloidal solutions obtained are indicated under each heading: detailed accounts of the method of preparation of typical solutions follow (see p. 14).

Ia. Chemical Reduction.

This general method of producing fine suspensions of metallic particles in water was really employed as early as 1750 in the case of gold solutions; at a later time silver solutions were made in an analogous manner. By the use of various reagents, such as hydrogen gas, carbon monoxide, phosphorus, etc., the salts of the metals, in quite dilute solution, are reduced so as to leave the pure metal in suspension. These gold and silver solutions offered a fascinating puzzle to chemists in the early part of the nineteenth century; probably Faraday was the first to give experimental evidence of the true nature of such solutions, a view amply justified by the ultramicroscope. Since the invention of the latter instrument and the widening of the interest in such solutions, the number of metals so reduced has greatly increased, as has also the number of the reducing agents employed for the purpose. On account of its historical importance, we shall outline one of Faraday's methods of producing gold sols, as adapted by Zsigmondy.

Reduction of Gold with Phosphorus (Faraday,[18] Zsigmondy [19]).

To 120 ccs. conductivity water (redistilled through a silver worm) are added 15 mgms. of gold hydrochloride

TABLE III.—PREPARATION OF AQUEOUS COLLOIDAL SOLUTIONS.

I. Condensation Methods.

- I*a*. Chem. reduction:
  - *Metals:* Au, Pt, Pd, Ir, Rh, Ru, Os, Ag, Hg, Bi, Cu, Se, Te.
- I*b*. Chem. oxidation:
  - *Elements:* S, Se, Te.
- I*c*. Hydrolysis:
  - *Oxides* or *Hydroxides:* Bi, Pb, Sn, Zr, Th, Ce, Tl, Fe, Cr, Cu, Ce.
- I*d*. Double decomposition:
  - *Acids:* Mo, Wo, Sn, Si.
  - *Sulphides:* As, Sb, Bi, Sn, Zn, In, Cu, Pb, Ag, Hg, Tl, Fe, Ni, Co, Mo, Wo, Au, Pd, Pt, Se, Te.
  - Various silver salts.
- I*e*. Schutzkolloide:
  - *Elements:* Au, Ag, Pt, Pd, Rh, Ru, Os, Hg, Se, Te, Ir, S.
  - *Iodides:* Ag, Pb, Hg.
  - *Metal sulphides.*
  - *Oxides:* Fe, Mn, Cu, Ag, Hg, Co, Ni, Bi.
  - Silver chromate and phosphate. Indigo.

II. Dispersion Methods.

- II*a*. Mechanical:
  - Grinding—Ultramarine.
  - Homogenizing of milk.
  - Slow diffusion—Clay.
  - (Solution of Emulsoids.)
  - Solution of dyes, soaps.
  - Natural gums dissolved in alcohol and added to water.
- II*b*. Electrical: Pulverization of elements under water: (methods of Bredig, Svedberg, Billiter), Au, Pt, Pd, Ir, Ag, Hg, Cu, As, Bi, Sb, Pb, Sn, Ni, Co, Mo, Wo, Ur, Fe, Va, Ta, Tl, Cd, Zn, Mn, Cr, Al, Ce, La, Mg, Cu, Sr, Ba, Li, Na, K, Rb, Cs, C, Si, S, Se, Te, P.
- Chemical
  - II*c*. Washing out electrolytes from precipitates:
    - *Elements:* Pt, Wo, B, Si, Zr.
    - *Oxides:* Sb, Si, Zr, Mn.
    - *Acids:* Mo. Va.
    - *Various metallic Sulphides*, e.g. Fe, Wo, Ir, Os, Cu.
    - Thallium iodide.
  - II*d*. Peptization:
    - As *oxides* or *salts:* Au, Cr, Mn, Mo, Ur, Wo, Va, Ta, Ni, Ti, B, Si, Th, Zr, Pt, Os, Ir, Sn, Al, Fe, Co, Cr, Yt.
    - *Sulphides:* Au, Cu, Cd, Hg, Fe.
    - *Ferrocyanides* of Fe, and Cu.

(crystals of $AuCl_4 . H . 3H_2O$) and 37 mgms. of the purest potassium carbonate. The gold chloride is reduced by about 0·5 ccs. of an ethereal solution of phosphorus, made by diluting a concentrated solution with five times its volume of ether. The formation of the hydrosol takes place slowly, the fluid becoming first bright brownish red, and then gradually bright red, often with a tinge of brown red, without showing the slightest turbidity in transmitted or reflected light. Particularly troublesome impurities in the water are the following: phosphates of the alkaline earths, silicates from the containing glass vessel, colloidally dissolved substances in ordinary commercial distilled water.

Ib. Chemical Oxidation.

This method is important on account of its use in the production of sulphur—a reaction employed by chemists for many years. The production of the hydrosol is more a matter of manipulation of an old experiment than any new development.

Colloidal Sulphur (Raffo [20]).

70 grms. sulphuric acid (d = 1·84) is placed in a cylinder of about 300 ccs. capacity, which is kept in cold water. A solution of sodium hyposulphite (50 grms. pure crystals in 30 ccs. distilled water) is added, drop by drop, while the acid is continually stirred. The hyposulphite must be added very slowly in order not to form too large masses of the insoluble sulphur, which is the end product of the reaction. When all the hyposulphite has been added, the whole is placed in a flask, 30 ccs. of distilled water added, the whole then shaken and heated on a water bath for about ten minutes at 80° C. At this temperature, the original turbid thick mass clears quickly and assumes the sulphur-yellow colour. The first purification consists in filtering the whole through glass wool in order to remove the undissolved sulphur. During the cooling the filtrate deposits the sulphur again; consequently it is set away in a cool place for some twelve hours. Heating and filtering is continued until all the insoluble sulphur is removed. The solution is then centrifuged, the sediment washed in a little

cold water, and then dissolved in as small a quantity of (hot) water as possible. The solution is neutralized by sodium carbonate which precipitates the greater portion of the sulphur, leaving a stable sulphur solution containing some sodium sulphate.

Ic. Hydrolysis.

By hydrolysis is meant the decomposition which many chemical compounds (soluble in water) undergo when dissolved in water. The action may be represented by the equation :—

$$\mathrm{Ct.An} + \mathrm{H_2O} \rightleftarrows \mathrm{H.An} + \mathrm{Ct.OH},$$

where Ct and An stand for the cation and anion respectively of the dissolved substance. When, in the course of the hydrolysis, a compound of small solubility with respect to the water is formed, conditions are favourable to the production of a colloidal solution.

Colloidal Thorium Hydroxide (Biltz [21]).

A solution of 7 grms. of [illegible] thorium nitrate in 50 ccs. water gives, after five days' dialysis, a hydrosol of thorium hydroxide as clear as water. While the water is in the dialyser only a very slight osmotic rise is observed. The reaction of the solution is neutral; with acidified ferrosulphate, nitrate can undoubtedly be recognized. Analysis gave 0·132 grms. thorium hydroxide per 100 ccs. of solution. Evaporation on a water bath leaves a gummy shining mass, which does not again dissolve in water. The colloidal solution is stable even after boiling.

Id. Double Decomposition.

Under this heading, following Svedberg,[15] we may include chemical condensation reactions which are not included under the three previous methods. They include the production of sulphides by the action of hydrogen sulphide on metallic solutions, of certain acids by the action of strong acids on salts, e.g. silicic acid by the action of hydrochloric acid on sodium silicate, etc.

Colloidal Metallic Sulphides (Linder and Picton[16]).

Solutions of metallic sulphides may be prepared in the following ways:—

1. A solution of the metallic salts is allowed to run into sulphuretted hydrogen water, kept saturated by a stream of gas. It may then be freed from uncombined hydrogen sulphide gas by a current of hydrogen, and dialysed to free it from salts.

2. The metallic hydrates are suspended in water and treated with hydrogen sulphide gas.

The solutions obtained contain hydrogen sulphide combined, and are, in fact, solutions of hydrosulphides.

By the first method one may obtain the solution of any metallic sulphide, provided no excess of acid be present. An arsenide, acidified with hydrochloric acid, if allowed to run into hydrogen sulphide water will readily give a solution containing about 5 grms. of sulphide per litre.

Ie. With Schutzkolloid.

Many substances added to pure water tend to retain any particles formed therein in a finely divided state of suspension. For example, if traces of gelatine be added to very dilute solutions of silver nitrate and potassium iodide, the insoluble silver iodide, obtained by mixing the solutions, remains in a state of fine suspension in the water. The gelatine seems to exert some sort of protecting action on the small particles, preventing their coalescence into larger masses. In addition to gelatine, gumarabic, water glass, dextrin, egg albumen, lysalbin acid, protalbin acid, starch, casein, and glycerine have served as the protecting or "schutz" colloid. The exact function of the *schutzkolloid* is one of the very perplexing problems of colloid chemistry.

Colloidal Silver Chromate in Sugar as the Schutzkolloid (Lobry de Bruyn,[22] Kuspert[23]).

The following solutions were used:—

1. Three of cane sugar of strengths: I, 65 per cent., II, 50 per cent., III, 25 per cent., respectively.

2. Tenth normal solutions of both potassium chromate and silver nitrate.

1 cc. of each of the chromate and nitrate solutions each diluted by the addition of 10 ccs. of pure water, gave, when mixed, a non-transparent, turbid solution which appeared reddish violet in transmitted light.

1 cc. each of the salt solutions were then diluted in turn by the addition of 10 ccs. of (1) sugar solution I, (2) sugar solution II, (3) sugar solution III, and then quickly and thoroughly mixed.

With I the reaction was somewhat slower than with pure water; there resulted a transparent red solution, with no apparent turbidity; in transmitted light there was no violet shown. A noticeable cloudiness appeared very slowly with standing.

Between II and III very little difference was shown; there appeared a turbidity at once, but much weaker than in the case of pure water. The transparency of the solution decreased on standing, much more rapidly than in the case of sugar solution I.

IIa. Mechanical Dispersion.

Mastic in Water.—As an example of the mechanical dispersion of a substance in water we may quote the usual method of producing hydrosols of many of the natural gums (such as mastic) which are themselves insoluble in water.[24] A small quantity of mastic gum may be easily dissolved in ethyl alcohol; a few drops of such a solution when mixed with, say, 100 ccs. of pure water gives a milky white permanent solution containing ultramicroscopic particles. The mastic content per cc. is very small, and the resulting hydrosol is exceedingly sensitive to the addition of electrolytes.

IIb. Electrical Pulverization.

It has long been known that an arc passing between metal electrodes causes the disintegration of the electrodes, and, as Faraday[18] showed, the metal is deposited in very fine particles. Bredig[25] first applied this to the manufacture of colloidal solutions by causing the arc to pass below the surface of distilled water contained in a vessel of clean, very insoluble glass or porcelain. He employed a current of from 4 to 10 amperes with a difference of potential at the arc of from 30 to 100 volts, and used as electrodes chemically pure metals. Care should be taken that electro-negative metals are not alloyed with electro-positive metals in the electrodes used. In practice the arc has to be made by some device giving intermittent sparking between the electrodes; by the use of a motor, various automatic arrangements may be made to serve the purpose. If contamination is rigidly avoided, the pulverized metal distributes itself through the liquid, giving rise to a transparent coloured solution which, in the pure state, will remain stable for any length of time.

The intensity of the current used in the Bredig method is harmful when the electrodes used are made of the softer metals, or when sols are attempted in organic liquids. For this reason, Svedberg [26] has made use of an oscillating discharge from an induction coil between specially constructed electrodes of the metals. The currents used were of the order of 10 milliamperes up to one or two amperes, the voltage being from 30 to 200 volts, so that the heating action of the spark was much reduced. By this means he greatly extended the number of both hydrosols and organosols produced electrically. (See also Morris-Airey and Long [27].)

Chemical Dispersion Methods.

In the two methods of preparation included under this heading, the substance to be produced in the colloidal state is first precipitated in an ordinary chemical reaction and the precipitate so treated as to induce its dispersion throughout the liquid media. In the first subdivision, the precipitant is freed from some coagulant (electrolyte) by washing with pure water; in the second, the reverse takes place — some electrolyte being added to the precipitate to bring the latter to the dispersoid state.

IIc. Washing of Precipitates.

Soluble Molybdanic Acid (Berzelius[28]).

This hydrate, e.g. precipitated from molybdan chloride by ammonia, is soluble in water. When one precipitates the acid with ammonia, one sees that at first the precipitate redissolves; finally this action ceases and the hydrate is then completely precipitated, because it is insoluble in water containing salts, particularly the ammonium salts. When these are eliminated by washing out the precipitate, the hydrate begins to dissolve again, and finally it completely dissolves to produce a reddish-yellow liquid—a hydrosol.

IId. Peptization.

By the addition of acids or alkalies to the precipitate (hydrogel) from some colloidal solutions, Graham[1] was able to bring the substance into the hydrosol state again. From the analogy between this action and the solution of insoluble colloids during the process of animal digestion, Graham called the above operation peptization. It is a method which has been employed with a great variety of reagents by many chemists since the time of Berzelius.

Colloidal Aluminium Oxide (Müller[17]).

50 ccs. of an aluminium chloride solution of 2·448 per cent Al_2O_3 content was placed in a flask, diluted with water and precipitated with ammonia at the boiling-point in the manner usually pursued in analytical chemistry. The solution was filtered and the precipitate carefully washed with hot water and then emptied into a flask to which some 250 ccs. of water was added. By means of a burette small quantities of 1/20 N hydrochloric acid solution were added and, after each such addition, the flask was again brought to the boiling-point, the water lost by evaporation being constantly supplied. The following phenomena were noticed: after the addition of the first traces of the acid, the precipitate was apparently unchanged; with further addition, it assumed a slimy consistency; finally, the point was reached where the original hydrogel

which lay at the bottom of the flask in masses, distributed itself in a completely uniform manner through the liquid, whereupon the latter assumed an opalescent aspect and passed easily and completely through a filter paper.

4. Classification according to Physical Properties.

The first attempt to classify colloids under this head is due to Hardy,[8] who divided all colloidal solutions into two classes which he called reversible and irreversible. Although not the original intention of Hardy, this division now depends on the characteristics of the dried residue left after evaporating the solution. If, as in the case of gelatine, the residue will dissolve again in water and reproduce the colloidal state, the solution is said to be reversible ; if, on the other hand, as in the case of the Bredig metal sols, the dried residue cannot be redissolved in the liquid so as to give the dispersoid, the solution is said to be irreversible. These two classes are almost, but not entirely, co-existent with those of the other classifications indicated in Table II. This classification contemplates dried residues. However, in the solutions of the irreversible class there are great differences of behaviour of the residue when the latter is not thoroughly dried. Some solutions, such as copper ferrocyanide, can be reproduced if, to the moist coagulum, a particular stabilizing ion be added ; in fact, the dispersion method of peptization is this operation on a moist coagulum. On the other hand, it is impossible to redissolve the coagulum from a Bredig metal sol, even if it is treated in the moist state.

A second characteristic by which these solutions may be differentiated is their action when electrolytes are added to them. "Colloidal solutions differ in their relation to small concentrations of salts, some, such as the hydrosols of metals, of silica and of alumina, are precipitated,—and others depend for their stability upon the presence of salts" (Hardy[8]) ; others, such as sols with *schutzkolloide*, do not seem to be affected by the addition of electrolytes. A close study of the methods of preparation suggests wide differences in the electrolytic content of different solutions, and consequent differences in their behaviour toward added electrolytes.

A third important physical property of the particles of the solutions is the sign of the charge which they bear. Solutions belonging to any sub-group might ultimately be divided into two sets, according to whether the particles are positively or negatively charged. No very exact rule may be laid down in this regard, except that, in general, oxides, hydroxides and sols of easily oxidizable metals usually have positively charged particles, while materials which do not easily oxidize give negatively charged particles. In the case of globulin, if the sol is acidic, the particles are positively charged ; if basic, negatively charged.

The behaviour of the suspensoids as to reversibility and irreversibility, and their sensitiveness to added electrolytes, leads us to a classification which may be useful in understanding colloidal solutions in general. As noted above, the emulsoids—solutions of such substances as gelatine, agar-agar, etc.,—need no further classification.

I. First, we may group together those which have the appearance of very fine suspensions of quite simple uniform particles ; they are noticeable in their extreme sensitiveness to added electrolytic solutions, and have usually a very low electrical conductivity. Under this class are included the Bredig metallic solutions, Zsigmondy's gold solutions, etc. They have in general a very small amount of the disperse phase present per cc. of solution ; Bredig sols have metal present to the order of 10 mgms. per 100 ccs.

II and III. Closely allied to those named above, we have a large class which depend for their stability upon a trace of salt absorbed by the colloidal particle. For example, Duclaux[29] prepared his solutions of colloidal copper ferrocyanide by the reaction of potassium ferrocyanide on cupric chloride and found that the colloidal particle (copper ferrocyanide) entangled a certain quantity of potassium ; as the percentage of potassium was decreased the stability of the colloid decreased, and the particles tended to coagulate when the potassium content was reduced to zero. The coagulating

TABLE IV.

Colloidal Solutions.

Suspensoids (Anhydrophilous).					Emulsoids (Hydrophilous).
Irreversible.			Reversible.		
	Stabilized by Entrained Ion.				
I. Low Content of disperse phase.	**II. High Content of disperse phase.**	**III. Peptizible.**	**IV. Mixtures of two colloids.**	**V. With Schutzkolloid.**	**VI. Emulsoids (Reversible).**
Bredig's sols. Faraday's Au. Zsigmondy's Au. Soaps. Dyes. Washed out precipitates. Alcoholic gum sols.	Globulin. Ferric HO. Sulphides. Silicic acid. Oxidation Colloids.	(Peptized colloids). Salicic acid. Stannic acid. Dialysed egg albumin. Oxides. Hydroxides. Some sulphides. Ferrocyanides of Cu and Fe. Ag I. (some).	Cassius Purple. Lottermoser Hg. Carey Lea's Ag. (some).	Ag I. Carey Lea's Ag. (some). Paal's gold. Mohlau's indigo. Oxides with sugar. Reduction colloids in sugar, starch, etc.	Gelatine. Gum-arabic. Agar-Agar.

power of electrolytes appeared to him to be due to the substitution of a new ion for the potassium of the particle, although it is not quite clear how this action results in coagulation.

As to additional members of this class we may cite the following facts :—

(*a*) Hardy gives the example of acid and alkali globulin as a true example of this class—the acid globulin retaining the negative radical of the acid, etc.

(*b*) The historically important ferric hydrate colloidal solution depends for its stability on a trace of the retained ferric chloride, as dialysis to remove the chloride brings about coagulation.

(*c*) Purified egg-albumen always contains chlorine enough to react on silver nitrate.

(*d*) Silicic acid nearly always contains traces of potassium, sodium, and hydrochloric acid ; continued dialysis produces coagulation.

(*e*) The metallic sulphides, e.g. arsenious sulphide and antimony sulphide, probably depend for their stability upon a slight trace of entrained hydrogen sulphide.

It is important to point out that in some cases, e.g. with copper ferrocyanide and silver iodide, after the coagulum [illegible] formed, addition of the particular stabilizing ion in certain concentration to the moist coagulum reproduces the colloidal solution and, [illegible] this account, these colloidal sols might be called reversible, if we change the definition of reversible to make it refer to the behaviour of the moist coagulum instead of dry residues. This leads to a subdivision of these suspensoids, stabilized by an entrained ion, into those perfectly irreversible and those reversible. Such colloidal solutions as the metallic hydrosulphides, ferric hydrate, etc., when once coagulated (or evaporated) cannot be changed back into dispersoids by the washing of the precipitate (or residue), or by the addition of stabilizing ions. On the other hand, the large number of colloidal solutions prepared by the method known as peptization are examples of the re-solution of a moist coagulum. Such solutions are those of silicic acid, various oxides and hydroxides, copper and iron ferrocyanides, silver iodide, etc. All the solutions of these two sub-classes have a much larger disperse phase content per cc. than the solutions of the first class.

IV. Cassius purple affords an example of what may really prove to be a large class; namely those solutions whose particles are really complexes of two different kinds of irreversible colloidal particles. "This purple, an apparently homogeneous gelatinous precipitate, was looked upon by Berzelius as a chemical compound of stannic acid, gold oxide and tin oxide, on account of its apparent homogeneity and its solubility in ammonia. Other authors called it a mixture of metallic gold and tin oxide. The formula which Berzelius adopted for his compound was in such good agreement with the analysis that there was no way of deciding the question analytically. It was first shown by synthesis of the gold purple from its components that it was not a chemical union but an intimate mixture of colloidal gold and colloidal stannic acid."[14] As in the case of silicic acid and stannic acid, which are changed from coagulum to solution by the addition of alkali, so also alkali added to the Cassius purple hydrogel (coagulum) reproduces the hydrosol state.

V. This sub-class owes its existence to the peculiar action of emulsoids and other substances on irreversible solutions. It is noted above that colloids of this latter class are, generally speaking, keenly sensitive to additions of comparatively small traces of electrolytes, while those of the former class remain in solution even in the presence of large quantities of electrolytic solutions. By adding a very slight trace of a reversible colloid, e.g., gelatine, to an irreversible colloid, the former acts as a protector to the particle of the irreversible colloid so that the latter is no longer coagulated by salts. Moreover, if the mixture be evaporated, the colloidal solution may be reproduced by dissolving in pure water. Gelatine added to the solution of sub-class (1) assumes the rôle of a protective colloid (*Schutzkolloid*). Gelatine added to solutions of silver nitrate and potassium iodide produces on mixing the two solutions a protected colloid, silver iodide; Carey Lea's silver, Paal's gold, Mohlau's colloidal indigo belong to this class.[14]

It is probable that the protecting substance forms a shell about the irreversible particles (Lecoq[20]); solutions of this sub-class then approach, in their properties, those of the emulsoid section.

In Table IV is arranged diagrammatically the foregoing classification, together with some examples of the solutions belonging to the various classes. From this classification one may expect great variety in the properties of the various colloidal solutions; the merging of one class into another makes any definite theory of the colloidal state a difficult matter.

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CHAPTER III.

THE ULTRAMICROSCOPE.

1. LIMITATIONS OF THE ORDINARY MICROSCOPE.

"THE history of the modern microscope, like that of nations and arts, has had its brilliant periods, in which it shone with uncommon splendour, and was cultivated with extraordinary ardour; these periods have been succeeded by intervals marked with no discovery, and in which the science seemed to fade away, or at least to lie dormant, till some favourable circumstance—the discovery of a new object or some new improvement in the means of observation—awaked the attention of the curious and reanimated the spirit of research."[1]

The ordinary microscope may be said to play two distinct roles in scientific investigation; first, it may be used to indicate the existence of minute, virtually self-luminous objects without giving one any direct evidence of their actual size, shape, or detail; and, secondly, as is more generally the case, it may be used to portray to us the real minute structure of the object—a circumstance which depends on the ability of the instrument to give distinct images of two points situated very close to one another.

A diagram of the course of light through the modern compound microscope illustrates the two phases in the development in construction during the whole history of the microscope, namely: (1) perfection of the methods of illumination most suitable to a given object, (2) the most advantageous transmission of the images formed to the observer's eye.

Up to about the year 1870, chiefly through the unfortunate lack of co-operation between manufacturing opticians and trained scientists, the advances made were, in the main, the results of random attempts to improve microscopic vision by perfecting objectives and varying the direction of the incidence of the illuminating pencil of light. Only when the manufacturing world began to appreciate the necessity of advancing along exact, scientific lines was the whole question of microscopic vision unified; to Professor Abbé, supported as he was by the faith of the glass manufacturer, we owe, more than to any other one man, the degree of perfection which has now been attained.

The increase in useful magnification possible with the microscope is subject to limitations which we may group into three classes:—

(1) Structural—corrections are necessary for such faults as spherical and zonal aberrations, chromatic aberration, and to fulfil conditions for the identity of position of the chromatic Gauss planes, the sine condition, etc. These corrections require the multiplication and spacing of the lenses used, which in turn involves losses of light by reflection and absorption.[2]

(2) Physiological—object glasses reach the limit of their useful development in the direction of increasing magnifying power so soon as, by the shortening of the focal length, the diameter of the object glass in its principal plane is reduced to something not much less than the diameter of the pupil of the eye. Object glasses can be made, and have been made, with as short a focal length as 1/50 in. (1/20 cm.), but they are mere curiosities, possessing no practical advantage over the 1/8, 1/10, or 1/12 in. in common use.[3]

(3) Diffractional—the phenomena of the diffraction of light really sets the limit to the resolving power of a given microscope and brings into prominence the numerical aperture of the objective, the method of illumination employed, and, as a consequence, the various immersion objectives.

Although the importance of the corrections for spherical and chromatic aberrations, and even the function of large aperture and immersion objectives, have been hinted at by early workers with the microscope (Hooke, 1665, and Martin, 1742, etc.), still the systematic attack on these difficulties did not materialize until the last century. Many manufacturers, both in England and on the Continent, continually strove to produce combinations of lenses of various shapes and of flint and crown glass such as would do away with spherical aberration and unite in one focus light of two different wave-lengths—so-called achromatic objectives. It had been suggested first [illegible] Sir David Brewster that "no essential improvement can be expected in the microscope unless from the discovery of some transparent substance which, like the diamond, combines a high refractive with a low dispersive power". Diamond ($n = 2{\cdot}417$) objectives were made by Pritchard in 1824, but, in addition to being a very refractory substance to work with, diamond almost invariably gave multiple images instead of a single one.[1] About 1875, in consultation with Professor Abbé and with the co-operation of Carl Zeiss, the glass firm of Schott & Genossen began an exhaustive series of experiments on the production of new crown and flint glasses which should combine high refractive with low dispersive powers. The net result, as regards microscope objectives, has been the production of the so-called apochromatic objectives, which have the following distinguishing characteristics: (1) the union of three different colours of the spectrum in one point of the axis, i.e. the elimination of the secondary spectrum left uncorrected for in the old achromatic objectives; (2) the correction for spherical aberration for two different colours instead of only one. On account of the hemispherical front lens, all objectives of considerable aperture exhibit chromatic difference of magnification, which has to be compensated for in the ocular. The fundamental point in this progress is that the necessity of empirical tests has been entirely obviated by precise mathematical computation of every detail of construction.

It was early found by practical opticians that the results obtained by using a powerful objective and a weak eyepiece were better than those obtained with a weaker objective and a more powerful eyepiece, although the theoretical magnification in the two cases might be the same. We now know that this difference is due to the larger numerical aperture possessed by the more powerful objective. The development of larger aperture worked along two lines, first merely improving the power of dry (air) objectives, and second, increasing the effective aperture of any given objective by the introduction of some liquid between the cover glass and the objective (so-called immersion objectives). The importance of large aperture and immersion objectives was vaguely suggested by Hooke, while definite instructions for what was practically an immersion objective were given by Brewster in 1812, and by Amici in 1815. Later both Goring and Lister reiterated definitely the necessity for a large aperture. About 1840 Amici used an oil immersion objective but did not work out the shapes of his lenses so as to correct for aberrations introduced by the oil. Various makers produced about the middle of the century very perfect water immersion objectives; in 1867, Hartnack and Praznowski obtained the prize at the World's Exposition at Paris for the best water immersion objective. The first scientifically corrected oil immersion objective was produced by Tolles of Boston in 1873.[4] The culmination of this work was the careful research of Abbé under the Zeiss firm, which resulted in the discovery of the unique properties of cedar oil (from *Juniperus virginiana*). Abbé's attention was probably drawn to the importance of a homogeneous immersion system by Stephenson, during the former's visit to London about 1875.[5] The advantages of the oil immersion bound up with the consequent increase in numerical aperture are: gain in illumination, freedom from cover glass correction, simpler correction for lenses, greater depth of focus, increased resolution.

The above mentioned visit of Abbé to London gave him the opportunity to introduce at first hand to an English audience his view of the function of the numerical aperture in contradistinction to the angular aperture of an objective, and his theory of the relation of diffraction to microscopic image formation. Unfortunately these views precipitated a schism in the ranks of English microscopists and delayed for many years English microscopic development which had been so marked from 1850 to 1875.

Parallel with the increase of numerical aperture and the adoption of immersion objectives, various methods of oblique illumination were devised. Oblique, or dark ground, illumination was used particularly in portraying line structures, the visible detail of which depended on the azimuth of the incident pencil. Such illumination was first suggested by Ross and Reade, but was brought into prominence by the extensive work of Wenham beginning about 1850. As we shall see, the invention of the ultramicroscopic method is, in a sense, a rediscovery of one or other of the various methods of dark ground illumination common among English microscopists in the seventies; indeed, many of the recently invented forms of ultramicroscopes are almost exact replicas of earlier forms of oblique illuminators. However, progress in illumination was not confined especially to oblique illumination; the study of the numerical aperture of the objective has brought into equal prominence the necessity of adjusting by means of a sub-stage condenser the ordinary illuminating cone. For the most efficient use of a given powerful objective, we must carefully arrange by means of the condenser the direction and aperture of the illuminating cone of light.

2. INVENTION OF THE ULTRAMICROSCOPE.

Naturally the progress in microscopy is the history of the two-fold attempt to push farther and farther the limits of (1) the small objects and (2) the minute detail, which can be revealed by the instrument. In the first case it is merely a matter of the intensity of the illumination of the small objects; the microscope would reveal to us the existence of a single molecule if it were possible to illuminate that molecule intensely enough. However, the problem of portraying minute detail is rather more important because it reduces itself essentially to that of distinguishing two neighbouring illuminated points. For although, given the illumination, we might see a single molecule, when we have a collection of molecules, or any small bodies, our ability to differentiate them depends on the distance between the neighbouring particles. This smallest limiting distance between two illuminated points in order that they may be just distinguishable, the limit of resolution of the microscope, has been worked out independently in two different ways by Helmholtz and Abbé.

In the work of Helmholtz the method followed is analogous to that used by Airy in treating of the same problem in relation to the telescope. It consists in tracing the image representative of a mathematical point in the object, the point being regarded as self-luminous. The limit of resolution depends upon the fact that, owing to diffraction, the image thrown even by a perfect lens is not confined to a point, but is spread over a patch or disk of light of finite diameter (called the spurious disk or the antipoint). Two points in the object can appear fully separated only when the representative disks are nearly clear of one another. The following method is given by Rayleigh[6] as a determination of the resolving power of an optical instrument for a self-luminous double point, applicable equally to the telescope and to the microscope.

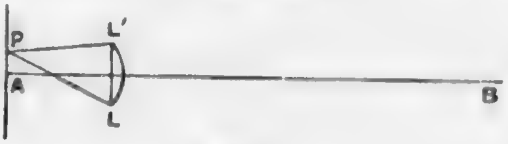

FIG. 1.

"In Fig. 1, AB represents the axis, A being a point of the object and B a point of the image. By the operation of the object glass LL′ all the rays issuing from A arrive in the same phase at B. Thus if A be self-luminous, the illumination is a maximum at B, where all the secondary waves agree in phase. B is in fact the centre of the diffraction disk which constitutes the image of A. At neighbouring points the illumination is less, in consequence of the discrepancies of phase which there enter. In like manner, if we take a neighbouring point P in the plane of the object, the waves which issue from it will arrive at B with phases no longer absolutely accordant, and the discrepancy of phase will increase as the interval AP increases. When the interval is very small the discrepancy of phase, though mathematically existent, produces no practical effect, and the illumination at B due to P is as important as that due to A, the intensities of the two luminous centre being supposed equal. Under these conditions it is clear that A and P are not separated in the image. The question is, to what amount must the distance AP be increased in order that the difference of situation may make itself felt in the image. This is necessarily a question of degree; but it does not require detailed calculations to show that the discrepancy first becomes conspicuous when the phases corresponding to the various secondary waves which travel from P to B range over about a complete period. The illumination at B due to P then becomes comparatively small, indeed for some forms of aperture, evanescent. The extreme discrepancy is that between the waves which travel through the outermost parts of the object glass at L and L′; so that, if we adopt the above standard of resolution, the question is, where must P be situated in order that the relative retardation of the rays PL and PL′ may on their arrival at B amount to a wave-length (λ). In virtue of the general law that the reduced optical path is stationary in value, this retardation may be calculated without allowance for the different paths pursued on the farther side of L, L′, so that its value is simply PL − PL′. Now since AP is very small, AL′ − PL′ is equal to AP . sin α, where α is the semi-angular aperture L′AB. In like manner, PL − AL has the same value, so that

$$PL - PL' = 2 \,.\, AP \,.\, \sin \alpha.$$

According to the standard adopted, the condition of resolution is therefore that AP, or ϵ, should exceed $\frac{1}{2}\lambda \div \sin \alpha$. If ϵ be less than this, the images overlap too much; while if ϵ greatly exceed the above value, the images become unnecessarily separated.

"In the above argument the whole space between the object and the lens is supposed to be occupied by matter of one refractive index, and λ represents the wave-length in the medium of the kind of light employed. If the restriction as to uniformity be violated, what we have ultimately to do with is the wave-length of the medium immediately surrounding the object. λ being the wave-length of the light in the medium in which the object is situated, if λ_0 be the wave-length in vacuum, $\lambda = \frac{\lambda_0}{\mu}$, μ being the refractive index of the medium; and thus

$$\epsilon = \frac{1}{2} \frac{\lambda_0}{\mu \sin \alpha}.$$

"In Abbé's method of treating the matter, the typical object is not a luminous point but a grating illuminated by plane waves. Thence arise the well-known diffraction spectra, which are focused near the back of the object glass in its principal focal plane. If the light be homogeneous the spectra are reduced to points, and the final image may be regarded as due to the simultaneous action of these points acting as secondary centres of light. It is argued that the complete representation of the object requires the co-operation of all the spectra. When only a few are present the representation is imperfect; and when there is only one—for this purpose the central image counts as a spectrum—the representation wholly fails.

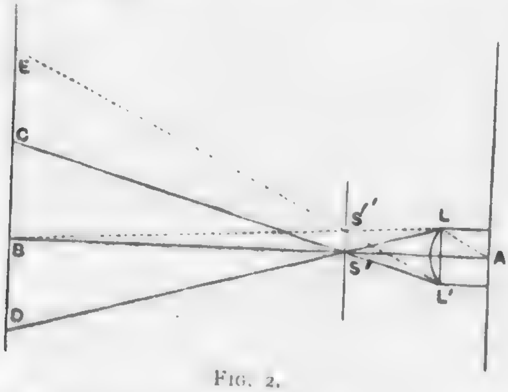

Fig. 2.

"That this point of view offers great advantages, at least when the object is really a grating, is at once evident. More especially is this the case in respect of the question of the limit of resolution. It is certain that if one spectrum only be operative, the image must consist of a uniform field of light, and that no sign can appear of the real periodic structure of the object. From this consideration the resolving power is readily deduced; we shall recapitulate the argument for the case of perpendicular incidence. In Fig. 2, AB represents the axis, A being in the plane of the object (grating), and B in the plane of the image. The various diffraction spectra are focused by the lens LL′ in the principal focal plane, S′ representing the central image due to the rays which issue normally from the grating. After passing S′ the rays diverge in a cone corresponding to the aperture of the lens and illuminate a circle CD in the plane of the image, whose centre is B. The first lateral spectrum S″ is formed by rays diffracted from the grating at a certain angle; and in the critical case the region of the image illuminated by the rays diverging from S″ just includes B. The extreme ray S″B evidently proceeds from A which is the image of B. The condition for the co-operation at B of the first lateral spectrum is thus that the angle of diffraction do not exceed the semi-angular aperture α. By elementary theory we know that the sine of the angle of diffraction is $\frac{\lambda}{\epsilon}$, so that the action of the lateral spectrum requires that ϵ exceed $\lambda / \sin \alpha$. If we allow the incidence on the grating to be oblique, the limit becomes $\frac{1}{2} \lambda / \sin \alpha$.

"We have seen that if one spectrum only illuminate B, the field shows no structure. If two spectra illuminate it with equal intensities, the field is occupied with ordinary interference bands, exactly as in the well-known experiments of Fresnel. And it is important to remark that the character of these bands is always the same, both as regards the graduation of light and shade, and in the fact that they have no focus. When more than two spectra co-operate, the resulting interference phenomena are more complicated, and there is opportunity for a completer representation of the special features of the original grating."

The Helmholtz-Rayleigh method treats of the diffraction as caused by the aperture of the objective, while Abbé deals with the diffraction due to the structure of the object. In presenting his view Abbé[7] says: "Every structural object, whether the structure is regular or irregular, which transmits or reflects a narrow-angled incident beam of light (or any number of such, making together a wide-angled cone), changes this beam, or each one of the several beams, into a wider or narrower pencil, with varying intensity in different directions, by virtue of diffraction. . . . It may be shown that the diffracted light emanating from the object may utilize the whole aperture of the system, although the incident cone of light, if it were simply transmitted in the absence of an object, would fill only a very small portion of the aperture."

The net result of the study of the limit of resolution gives

$$\epsilon = \tfrac{1}{2} \lambda_0 / \text{N. A.}$$

as the necessary and sufficient distance by which two points must be separated in order that they may be distinguished by a microscope of numerical aperture N. A. by means of light of wave-length λ_0. Manifestly the two ways of reducing the value of ϵ are: (1) decreasing λ_0, (2) increasing N. A. λ_0 may be reduced by the employment of ultraviolet light which, in conjunction with fluorite lenses, first used by Spencer (America), in 1860,[4] is practically only feasible in microphotography. The increase in N. A. ($= \mu \sin a$), involves increase in μ and $\sin a$. The Zeiss firm have exerted every effort to take complete advantage of these increases. By the manufacture of special glasses, a has been increased to 73^0 ($\sin a = ·95$), while by the use of immersion objectives, the value of μ is as follows: water 1·33, cedar oil 1·515, monobromonaphthaline 1·66. The greatest value of the numerical aperture obtainable is virtually 1·53.

The maximum value of N. A. will give for the necessary interval between two luminous points for such a microscope: $\epsilon = 0·327 \lambda_0$. Table V shows the theoretical value of this interval and the limiting value of the number of lines per cm. and per in. to such a structure as a grating.

TABLE V.—MAXIMUM LIMIT OF RESOLUTION FOR THE FRAUNHOFER LINES.

Line	Wave-length.	Interval in cms.	Lines per cm.	Lines per inch.
A	7594 Å.U.	$2·48 \times 10^{-5}$	40300	102,700
B	6867 ,,	$2·25 \times 10^{-5}$	44400	113,200
C	6563 ,,	$2·15 \times 10^{-5}$	46500	118,500
D_1	5896 ,,	$1·93 \times 10^{-5}$	52000	132,600
E	5270 ,,	$1·72 \times 10^{-5}$	58400	148,900
F	4861 ,,	$1·59 \times 10^{-5}$	62900	160,400
G	3969 ,,	$1·30 \times 10^{-5}$	76900	196,100

The highest numerical aperture (with homogeneous immersion) catalogued by Zeiss is 1·40, so that the maximum number of lines per cm. (or inch) will be reduced in the proportion of 1·53 to 1·40. With an immersion objective of N. A. 1·35 and an immersion condenser of 1·30, both carefully adjusted and with useless light excluded by a suitable stop, Johnstone Stoney[8] found that the practical limit of proximity at which particles in a row may be placed consistently with our seeing them as separate objects (with wavelength 0·45 μ), is somewhere about 0·20 μ or 0·19 μ, i.e. 2·0 or $1·9 \times 10^{-5}$ cm. or about 1/130,000 of an inch. He has also shown that a pair of objects can be seen as two, when distant from one another about $\frac{5}{8}$ of the interval at which a row of such objects must be spaced in order to make it possible to resolve them with a given microscope. Again, as shown by Gordon,[3] if an object of uniform structure be illuminated by light which is already diffracted, the resolution is much better than for ordinary illumination.

While the above limit is in reality the limit of the interval between two points which may just be differentiated and does not represent the limit of smallness of particles just visible, it may be looked upon also as the limit of small particles for which it is possible to detect any detail by microscopic vision. The attempt to advance our knowledge of still smaller particles led to the invention of the ultramicroscope.

The prominence given in recent years to colloidal substances has created the desire to render visible finer and finer particles. The true nature of such substances in very finely divided state was forecasted by Faraday in his work on gold ruby glass and colloidal gold solutions. At the Royal Institution in 1856,[9] Faraday "had been led by certain considerations to seek experimentally for some effect on the rays of light, by bodies which when in small quantities had strong peculiar action on it, and which also could be divided into plates and particles so thin and minute as to come far within the dimensions of an undulation of light, whilst they still retained more or less of the power they had in mass. . . . When a solution of gold is placed in an atmosphere of phosphorus vapour the gold is reduced, forming films that may be washed, and placed on glass without destroying their state or condition. . . . When gold wires are deflagrated by the Leyden discharge upon glass plates, extreme division into particles is effected, and deposits are produced, appearing by transmitted light, of many varieties of colour, amongst which are ruby, violet, purple, green, and grey tints. By heat many of these are changed so as to transmit chiefly ruby tints, retaining always the reflective character of gold. . . . If a piece of clean phosphorus be placed beneath a weak gold solution, and especially if the phosphorus be a clear thick film, obtained by the evaporation of a solution of that substance in sulphide of carbon, in the course of a few hours the solution becomes coloured of a ruby tint; and the effect goes on increasing sometimes for two or three days. At times the liquid appears clear, at other times turbid." Faraday believed "this fluid to be a mixture of a colourless, transparent liquid, with fine particles of gold. By transmitted light it is of a fine ruby tint; by reflected light, it has more or less of a brown yellow colour. That it is merely a diffusion of fine particles is shown by two results; the first is, that the fluid being left long enough the particles settle to the bottom; the second is, that whilst it is coloured or turbid, if a cone of sun's rays (or that from a lamp or candle in a dark room) be thrown across the fluid by a lens, the particles are illuminated, reflect yellow light, and become visible, not as independent particles but as a cloud. Sometimes a liquid which has deposited much of its gold remains of a faint ruby tint, and to the ordinary observation, transparent; but when illuminated by a cone of rays, the suspended particles show their presence by the opalescence, which is the result of their united action. . . . Some specimens, however, of the fluid, of a weak purple or violet colour, remain for months without any appearance of settling, so that the particles must be exceedingly divided; still the rays of the sun or of a candle in a dark room, when collected by a lens, will manifest their presence. The highest powers of the microscope have not as yet rendered visible either the ruby or the violet particles in any of these fluids. . . . Glass is occasionally coloured of a ruby tint by gold; such glass, when examined by a ray of light and a lens, gives the opalescent effect described above, which indicates the presence of separate particles. It becomes a question whether the constitution of the glass and the ruby fluids described is not, as regards colour, alike. Whether the gold is in the state of the pure metal, or of a compound, has yet to be decided. It would be a point of considerable optical importance if they should prove to be metallic gold; from the effects presented when gold wires are deflagrated by the Leyden discharge over glass, quartz, mica, vellum, and the deposits subjected to heat, pressure," etc., Faraday inclines to believe that they are pure metal. The determination of the exact structure of these particles presented itself to Zsigmondy almost fifty years later; the method of rendering them visible, inaugurated and perfected by Zsigmondy and Siedentopf,[10] is essentially a refinement of the rough method used by Faraday himself. Whereas Faraday was enabled to recognize only the cloud of particles, Siedentopf and Zsigmondy, by elaborate illumination and the application of the microscope, succeeded in making individual particles visible.

Since the original Siedentopf and Zsigmondy ultramicroscope was brought out, many other forms of ultramicroscopes have been invented, or rather re-invented; the underlying principle of all forms of the instrument is the same; the whole purpose of the ultramicroscope is to render the particles so self-luminous, in contrast to a dark background, that they may be seen as points of light by an ordinary microscope. In the discussion of the various forms it is necessary to differentiate the two beams of light involved, viz.:—

1. The illuminating bundle of rays.
2. The image forming bundle of rays.

The incident illuminating rays are never allowed to enter the objective; the particles are rendered visible by the light which they scatter out of the main illuminating beam. This result is obtained, with varying success, in one of the four following ways:—

I. Orthogonal illumination—the particles viewed by a microscope the axis of which is at right angles to the direction of the illuminating beam (Fig. 3).

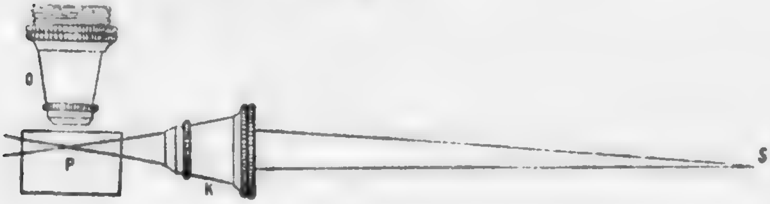

Fig. 3.

II. Oblique illumination, arranged either by the incident direction or by means of internal reflections so that no direct light enters the objective (Fig. 5).

III. Oblique illumination by an axial beam through a sub-stage condenser with central stop, or through a specially constructed, reflecting condenser provided with central stop (Fig. 6).

IV. Axial illuminating beam with small aperture and direct light cut out by means of a stop back of the objective.

I. Orthogonal Illumination.

The slit ultramicroscope of Zsigmondy and Siedentopf is the outstanding example of the successful application of this form of illumination and vision. The following is Zsigmondy's description[11]:—

"The solar rays reflected from a heliostat enter the darkened laboratory through an iris diaphragm. In the room is an optical bench about 1·5 metres long, having a metal flange, P (Fig. 4), supported on an adjustable stand G. . . .

"On this, by means of carefully adjusted brackets, are mounted the individual parts of the apparatus. The light rays first enter the telescope objective F_1, having a focal length of about 10 mms., which throws an image of the sun about 1 mm. in diameter on a finely adjusted slit head S, which is modelled after Engelmann's microspectral objective.[12] By the horizontal bilateral slit, this image can be reduced to 5 – 50 hundredths of a millimetre, as desired. The width of the slit may be read off from an index on the drum connected with the screw. The edges limiting the height of the slit are movable horizontally, and may be placed from 1/10 to 2 mms. apart. A polariser N may be placed behind the slit when desired. The iris diaphragm J shuts off any side-light which may be reflected from the edges of the slit. By means of the chisel-shaped diaphragm B one-half of the beam of light may be cut off; this is necessary when immersion objectives are used, in order to prevent objectionable reflection from the mounting of the front lens, due to the closeness of the objective. A second telescope objective F_2 of 80 mm. focal length forms a quarter-size image of the slit at the focal plane E of the condenser K. By means of the microscope objective AA, used as a condenser, this picture E (reduced to $\frac{1}{8}$ its size) is projected into the preparation. It should be seen that full use is made of the aperture of the condenser system K, by controlling the illumination of its rear focal plane. The upper half of the rays emerging from the objective AA are cut out when the picture of the semi-diaphragm B, thrown by the telescope objective F_2 into the after-focal plane of AA, darkens the upper half of this plane

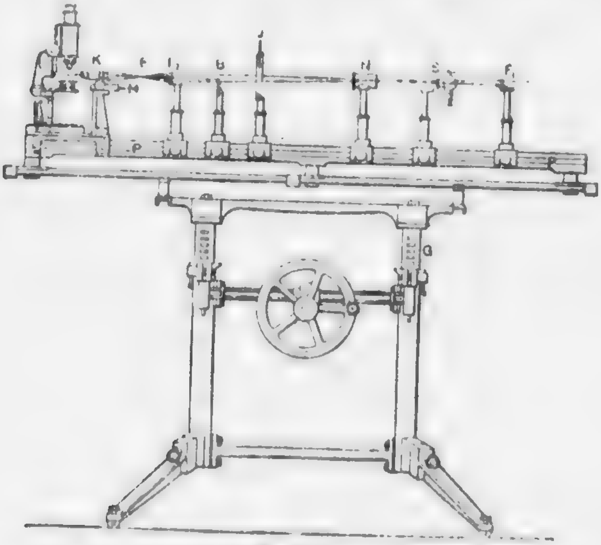

FIG. 4.

By means of two micrometer screws, working in a horizontal plane, and perpendicularly to each other, the condenser-objective may be readily centred in the optical axis of the microscope proper."

By means of this apparatus the particles in a very shallow layer of the specimen—solid or liquid—are intensely illuminated by sunlight (or arc lantern) and none of the direct illuminating rays reach the eye.

II. SIMPLE OBLIQUE, NON-AXIAL ILLUMINATION WITHOUT CENTRAL STOP.

It had been noticed by English microscopists early in the last century that the resolving power of an objective increased with the obliquity of the illuminating beam. By gradually increasing the obliquity it was noticed that the microscopic picture suddenly changed completely; it became bright on a dark ground instead of dark on a bright ground.[13] This led to the development of the so-called dark-ground illumination. Table VI shows the chronological development of the simplest form of dark-ground illumination, adapted first to ultramicroscopic purposes by Cotton and Mouton. The object is illuminated by a beam incident in such a

TABLE VI.—OBLIQUE ILLUMINATION WITHOUT CENTRAL STOPS.

No.	Year.	Experimenter.	Method.	References
1	1793	Dellebare.	By system of mirrors.	14
2	1838	Rev. J. B. Reade.	Single plano-convex lens.	15, 16, 17
3	1856	F. H. Wenham.	Lens, amici prism, total reflection prism.	15, 18, 1
4	1856	F. H. Wenham.	Half prism and lens.	15
5	1869	F. H. Wenham.	Half cylinder, lens and mirror.	15, 20
6	1877	J. J. Woodward.	Same principle as in No. 2.	15, 21
7	1881	Hyde.	Same principle as in No. 3.	15, 19
8	1903	Cotton-Mouton.	Internal reflection in glass block.	15, 22
9	1905	O. Scarpa.	Same principle as in No. 2.	15, 23

direction as to be out of line of the aperture of the objective, and usually totally reflected at the under side of the cover glass in order not to enter the objective. The illuminating source is brought to a focus as nearly as possible at the point of total reflection, at which point the specimen is placed; as particles are brought into the path of the light at the point of total reflection, some of the light which they scatter passes into the microscope. As the principle involved in all these cases is the same, it will probably suffice to describe the apparatus of Cotton and Mouton.

The diagram, Fig. 5[22, 24], exaggerates the relative sizes of the smaller parts of the Cotton-Mouton apparatus. A drop of the solution to be examined is enclosed beneath a thin cover glass on a microscopic slide. The plate is placed on a special block of glass, ABCD, good optical contact being made by an intervening thin layer of cedar oil, the refractive index of which does not differ much from that of glass. The block ABCD (for which a Fresnel rhomb serves very well) allows the direction of a beam of light to be adjusted easily so that, after being internally reflected at the under surface (CD), the succeeding internal reflection at the upper surface may be made to take place at the critical angle

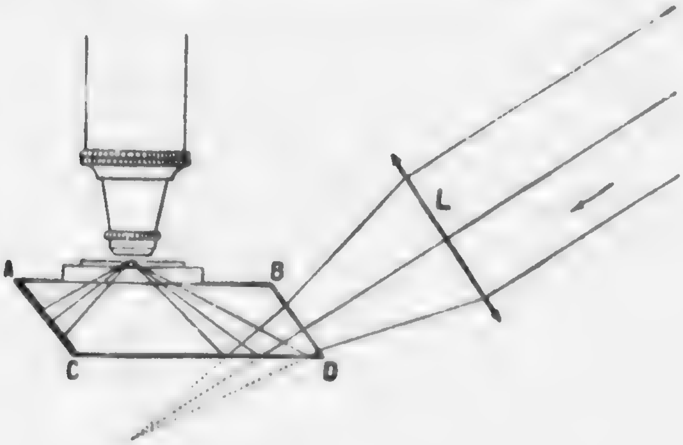

Fig. 5.

The proper adjustment of the lens L and the block allows the beam to come to a focus just at the drop of the liquid. As the particles in the solution come into the path of the beam, the light striking them is now no longer totally reflected, but is scattered into the microscope. As the field of view is otherwise dark, the appearance is that of a dark sky filled with moving stars—the Brownian movement being at once recognizable.

III. OBLIQUE ILLUMINATION FROM AXIAL BEAM BY MEANS OF SUB-STAGE CONDENSER WITH CENTRAL STOP.

The forms of dark-ground illumination given in the above class have the disadvantage that the illuminating system is not made a simple attachment to the microscope stage. Wenham and others remedied this defect in their forms of co-axial dark-ground condenser; the various forms are indicated in Table VII.

TABLE VII.—OBLIQUE ILLUMINATION WITH SUB-STAGE CONDENSER.

No.	Year.	Experimenter.	Method.	References
10	—	Th. Ross.	Spot lens.	15, 1, 16
11	—	Nachet.	Prism with multiple reflections.	25
12	1850	Wenham.	Two Nachet prisms and lenses.	15, 26
13	1850	Wenham.	Hollow reflecting paraboloid and spot lens.	15, 1, 26
14	1852	Shadbolt.	Annular condenser.	15, 16, 27
15	1854	Wenham.	Solid paraboloid and stop.	15, 1, 28, 29
16	1855	Nobert.	Truncated plano-convex lens.	15, 16
17	1856	Wenham.	Solid paraboloid and spot lens.	15, 18, 1
18	1856	Wenham.	Solid truncated paraboloid.	15, 18, 1
19	1861	Rev. J. B. Reade.	Hemispherical lens with spot.	30
20	—	J. Mayall.	Semi-cylinder and spiral diaphragm.	1
21	1872	Wenham (Wells).	Reflex illuminator.	15, 31, 32, 33
22	1876	Nachet.	Glass truncated cone.	15, 34
23	1877	J. Edmunds.	Solid truncated cone and revolver.	15, 35
24	1877	Stephenson.	Catoptric illuminator.	15, 36
25	1878	J. Woodward.	Truncated right-angled prism.	37
26	1879	Stephenson.	Catadioptric immersion illuminator.	15, 38
27	1883	Abbé.	Sternblende Kondensor.	
28	1906	Heimstadt.	Similar to No. 24.	15, 39
29	1907	Riechert.	Similar to No. 22.	15, 40
30	1907	Siedentopf.	Paraboloid condenser (Nos. 18, 23).	41
31	1908	Ignatowski.	Bispherical condenser.	42
32	1910	Siedentopf.	Cardioid condenser.	43
33	1910	Jentzsch.	Concentric condenser.	44

It will be noticed that some of the earliest of these forms are quite identical with the most recent. Originally they were used for oblique illumination of ordinary microscopic material, and were replaced, under the advice of Abbé, by the central stop accessory on the ordinary condenser. This condenser afforded an easy method of varying at will the obliquity and the aperture of the illuminating beam. It was forgotten that the older forms possess the advantage of colour-free, oblique illumination and, consequently, for the special aim of dark-ground illumination, are superior to Abbé's central stop condenser.[15]

In the methods of oblique illumination given under the second class (Table VI), the appearance of the object depended on the azimuth of the incident light. In order to make the illumination more uniform, Edmunds[35] arranged to have the light fall on the object from four sides. Early in his work Wenham, by the use of the paraboloid, produced uniform illumination in all directions. The principle of these methods is shown in Fig. 6 (Paraboloid, Wenham-Siedentopf).

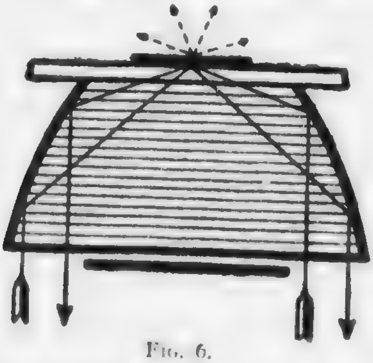

FIG. 6.

The incident light, reflected by the plane microscope mirror, has its central portion screened off, while the outer rays are brought by a series of reflections to be focused on the object where they are internally reflected as nearly as possible at grazing incidence. As the fine particles come into the path of the light, they scatter part of the light into the microscope, as in the case described above.

As in all forms of ultramicroscope, the aim here is to illuminate the particles as intensely as possible, relatively to their background. This requires (1) the aperture of the illuminating cone of light to differ as greatly as possible from that of the image-forming cone, (2) the light source to be exactly focused at the point of the specimen under observation, i.e. perfect union at a point A of the rays of the illuminating pencil (Fig. 6), (3) the condenser to be free from spherical difference of magnification, i.e. fulfilment of the sine condition.[42] These ideals have led to the improvements recently suggested by Siedentopf, Ignatowski, and Jentzsch.

IV. AXIAL ILLUMINATION WITH CENTRAL STOP BACK OF THE OBJECTIVE.

In this case the axis of the illuminating cone of light and that of the rays diffracted by the object are in the same straight line, and not inclined at a great angle to one another, as in the other methods. The direct illuminating rays are stopped out either by a carefully centred stop behind the objective, or by a method, suggested by Abbé,[43] by which a stop is formed by grinding flat and blackening a small central portion of the curved surface of the front lens of the objective. The portion ground away is exactly calculated to suit the aperture of the illuminating objective (condenser). This method obviates difficulties of centring and prevents decentring, while at the same time the objective may be used for observation in the ordinary way without dark-ground illumination. The difficulty which has thrown this method of dark-ground illumination into disuse, is that the central screen changes destructively the distribution of the brightness in the diffraction fringes, as pointed out by Siedentopf[45] and Jentzsch.[44]

3. LIMITATIONS OF THE ULTRAMICROSCOPE.

Lord Rayleigh[46] has shown that the intensity of the light diffused from a particle, small in all dimensions in comparison with a wave-length of light, varies directly as the quantity (p. 101):

$$\left|\frac{\mu'^2}{\mu^2} - 1\right|^2$$

where μ and μ' are the indices of refraction of the medium and the particle respectively. On account of this factor one cannot set a definite limit to the smallest particle visible by means of the ultramicroscope; if the index of refraction of the particles is very nearly the same as that of the surrounding liquid, they will remain invisible, no matter what the intensity of the illuminating pencil. Thus small particles of gold, silver, and copper in their colloidal mixtures are easily visible because the refractive indices of these metals are greatly different from that of the medium in which they are embedded, while in the case of colloidal solutions of such substances as silicic acid, oxide of aluminium, and albumen, the particles are not easily visible on account of the very slight differences between the indices of refraction of these substances and that of water.[13]

However great the difference between the refractive indices of the particles and the medium, there is a lower limit to the size of the particles which can possibly be made visible, due merely to the intensity of the illumination. In Table XVI (p. 117) is recorded the difference in size between the smallest gold particles visible to Zsigmondy [10, 11] with arc-light illumination and sunlight illumination. As pointed out by Siedentopf,[13] single molecules could be rendered visible if they could be separated sufficiently from their neighbours and illuminated intensely enough; however, the illumination necessary in this case would have to be so strong as to be quite beyond the possibility of attainment.

The smallest particle of gold observed by Zsigmondy, using sunlight illumination, was $1{\cdot}7 \times 10^{-7}$ cm. in diameter. Keeping in mind the favourable circumstance of the large difference of index of refraction between gold and water, we may cite this as the smallest particle ever observed.

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CHAPTER IV.

THE BROWNIAN MOVEMENT.

1. Historical.

This discovery of Brown[*] [1] was really a development from the observations of the movements of microscopic animalcules in various liquid media. We have references to such observations as far back as Leeuwenhoek (1632-1723), Stephen Gray (*d.* 1736), and Comte de Buffon (1707-1788). Up to 1827 many microscopic objects suspended in water had been observed to be in rapid motion, but this phenomenon was supposed to be connected always with living matter. This view was disproved by Brown's series of experiments. He began by mixing in water pollen from ripe anthers of Clarckia Pulchella and from those of Onagrariæ Œnothera and observed that the pollen appeared as very minute spherical bodies which were in rapid motion in the liquid—a phenomenon of pollen dust already known to Needham and Gleichen. In order to prove whether or not this motion was a phase of life, Brown examined for similar action the spore dust of mosses and equiseti that had been dry for a century. Surprised to find just as lively a motion with these, he tested, in finely divided state in water, such inanimate substances as gums, resins, wax, coal, glass, rocks, manganese, lead, bismuth, nickel, antimony, arsenic, and sulphur. He found the same unique motion in every case; his conclusions may be summed up best in his own words.

"Extremely minute particles of solid matter, whether obtained from organic or inorganic substances, when suspended in pure water or some other aqueous fluids, exhibit motions for which I am unable to account and which from their irregularity and seeming independence resemble in a remarkable degree the less rapid motions of some of the simplest animalcules of infusions. The smallest moving particles observed, and which I have termed active molecules, appear to be spherical, or nearly so, and to be between 1/20,000th and 1/30,000th of an inch in diameter; other particles of considerably greater and various size, and either of similar or of very different figure, also present analogous motions in like circumstances.

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[*] An interesting reference is made to Brown's paper in George Eliot's story, "Middlemarch," Book II, chap. XVII.

"I have formerly stated my belief that these motions of the particles neither arose from currents in the fluid containing them, nor depended on that intestine motion which may be supposed to accompany its evaporation.

"These causes of motion, however, either singly or combined with others—as the attractions and repulsions among the particles themselves, their unstable equilibrium in the fluid in which they are suspended their hygrometrical or capillary action, and in some cases the disengagement of volatile matter, or minute air bubbles—have been considered by several writers as sufficiently accounting for the appearances. Some of the alleged causes here stated, with others which I have considered it unnecessary to mention, are not likely to be overlooked or to deceive observers of any experience in microscopical researches: and the insufficiency of the most important of those enumerated may, I think, be satisfactorily shown by means of a very simple experiment (referring to evaporation)."

Although, as is indicated by the above extract, the questions underlying this phenomenon are to a great extent physical in their nature, physicists do not seem to have attacked them for a great many years after Brown's work was published. About 1868, some experiments, which were in a sense a repetition of those of Brown, were reported to the Manchester Philosophical Society by Dancer[2]: the new facts which he brings out are that gamboge in water gives good results and that the smallest globules of oil in milk show the Brownian movement. At about the same time before the same Society, Jevons[3] communicated the results of his epoch-making experiments. Briefly, his conclusions are as follows: (1) repeating Brown's observations with many subtances, he finds that the motion depends on the size of the particles and very little, if any, on the nature of the material in the particles: (2) with powdered clay or glass, in water, the motion seems to exist parallel with the stability of the suspension: (3) pure water gives the best movement, while addition of salts usually causes its cessation: (4) the action of acids, alkalies, and salts seems to be independent of their chemical constitution: (5) ammonia and boracic acid do not affect the motion, acetic acid stops it, while sodium silicate seems to increase it: (6) albumen, dextrin, cane and grape sugar, starch, and alcohol seem to have little effect, while gum arabic increases the motion and the stability of the solution. His work on the effect of added electrolytes led Jevons to ascribe the stability of the particles to their possession of electrical charges.

On the continent these phenomena were being investigated by Wiener, Exner, and Schultze, who also tried to single out the cause of the motion from among the various explanations offered. A résumé of their work is to be found in the Jahresberichte of 1867, as follows:—

"Chr. Wiener instituted microscopic observations of these movements, and came to the conclusion that this trembling, irregular, unsteady motion of solid molecules, which alter their direction in the briefest fraction of time in their zig-zag course, has for its basis the continual movements which, by virtue of their molecular constitution, belong to fluids. He learned through his investigations that (1) the movements are not those of infusoria; (2) the movement is not communicated to the fluid; (3) the trembling movement is not in any way derived from the varying attraction or the collisions of the various oscillating molecules; (4) the movement is not derived from changes in temperature; (5) the movement is not derived from evaporation. Consequently, there remained, in his opinion, nothing to account for the peculiar movements but the property of the fluid itself. This explanation received direct confirmation from Wiener's observation, that the speed of the movement has a certain relation to the size of the molecule. Lately S. Exner has extended the investigations of Wiener. Exner sought to test with reference to the molecular motion whether or not either chemical causes or mechanical ones, such as pressure, vibration, and so forth, could in any way produce an acceleration or a retardation of the effect. Only by exposure to light and heat did the motion become accelerated, and then in such a manner as, in the case of glycerine, to give freer motion to the molecules on account of decreasing the viscosity of the liquid. Exner also examined into the properties of fluids in which solid molecules remain suspended. The results of his investigation resolve themselves into the following points: (1) the liveliness of the molecular movement is heightened by light and heat, and by radiant as well as by conducted heat; (2) one of the consequences of the molecular movement is, that the molecules, in a specifically lighter fluid, not only do not sink to the bottom, but overcome the force of gravitation to such a degree as to spread themselves equally throughout the fluid; (3) the velocity of this scattering is influenced by light and heat. It should be mentioned here that Fr. Schultze had already stated that substances, when most finely divided, especially such as seemed under the microscope to be amorphous, and exhibited the Brownian movements, remain suspended in pure water and in many other fluids for days, weeks, and months at a time, so that the fluid containing them presents a cloudy or at least an opalescent appearance."

Wiener [4] and Exner [5] are the first to give definite figures for the velocities with which particles of various sizes move (see Table VIII).

Gouy [6] extended the number of suspensions viewed and also contributed extensively to the experimental work determining the cause of the motion. Reserving until later the experiments bearing on the theory of the motion, we may note here that he observed that the Brownian movement was shown by mineral and organic particles in water, salt solutions, acids, alcohols, ethers, hydrocarbons, oils and glycerine, and found that in general electrolytes added to aqueous solutions caused cessation of the movement and coagulation. As a result of his many experiments, he was driven to ascribe the motion to the thermal vibrations of the molecules of the liquid.

Ramsay [7] and Cantoni [8] disagree with the statements of Jevons and Gouy that the velocity of the particles in aqueous solutions does not depend on the material of which the particle consists, but merely on the size of the particle Ramsay says that the velocity depends on the size and density of the particles: he thinks that the particles in pure water do not touch one another at any time and, in fact, that they do not appear to influence one another in their motion. Spring[9] also believes that, when the particles appear to collide, they do not touch one another, as each particle in pure water is surrounded by a special liquid layer which is destroyed only by the addition of electrolytes. In fact it seems that neighbouring particles do influence one another (see Zsigmondy[10]); this view was also put forward by Maltezos.[11] The latter points out that the movement is complex, consisting of the ordinary zig-zag motion which he calls Brownian alone, a vibration about a line and a rotation. He also states that the general action of added electrolytes causes a retardation of the motion and gives evidence of the presence of ultramicroscopic particles in the solutions which he examined—ordinary water containing a trace of dirt or highly diluted ink.

The above outline brings us to the time of the invention of the ultramicroscope, which afforded most valuable information regarding the motion of the very fine and, consequently, fast moving ultramicroscopic particles. Recently the first reliable velocity measurements have been made, but these can best be dealt with in examining later the confirmations of the kinetic theory of the Brownian movement.

2. Samples of Solutions in which the Brownian Movement may be observed.

1. Gamboge, as prepared by Perrin,[12] has the advantage of giving both microscopic and ultramicroscopic particles. It is made by the desiccation of the milk secreted by a guttiferous plant from Indo-China. A part of the dry residue is rubbed under distilled water, in the manner of making soapy water; the gamboge dissolves giving a yellow solution containing spherical particles of various sizes. Or, the yellow dry residue may be completely dissolved in alcohol, giving rise to a transparent true solution. This alcoholic solution, when

poured quickly into a large excess of pure water, produces an emulsion with spherical grains. One can separate these grains by centrifuging from the alcoholic water which contains them and then dilute them in excess of pure water, a process resulting in an emulsion with grains of different sizes, usually of diameter less than 10^{-4} cm.

2. Spring[9] prepared mastic solutions in a manner analogous to the preceding. 4 grams of mastic were dissolved in 100 ccs. of alcohol; 10 ccs. of the alcoholic solution were stirred slowly into a litre of pure water and the whole was filtered. This gives a solution with various sized particles.

3. Meade Bache[13] finds that a solution containing carmine from cochineal gives much more brilliant particles than gamboge, or, one would gather, than mastic. It contains very brilliant microscopic particles which show much better with weak illumination than do the particles of gamboge. "With a weak aqueous solution of carmine one may see by daylight on a background of faint blue, or with artificial light on a golden background, thousands of tiny particles, bright as sparks of ruby, shimmering and performing their independent evolutions over the field of view."

4. Zsigmondy[10] and Svedberg[14] and others have observed the movement of the particles in the solutions made by the methods recorded in chapter II.

3. VELOCITIES OF PARTICLES OF VARIOUS SIZES.

In Table VIII are arranged the various determinations of the velocities of particles of various sizes in different solutions. The names of the observers are placed in chronological order and, naturally, greater weight must be accorded to the later results.

The experiments of Exner, Wiener, and Ramsay were carried out before the ultramicroscope came into use and consequently deal only with particles above 10^{-5} cm. diameter. Their measurements were made apparently with a micrometrically divided glass scale and watch.

As is pointed out by Zsigmondy, the absolute motion of the particles is very hard to observe directly, although differences in motion may be recognized very easily. The difficulties of direct observation have been overcome by the application of the cinematograph to the microscope by Victor Henri.[15] The latter made with each solution examined, a series of exposures each of duration of 1/320th of a second at intervals of 1/20th of a second, and was thus enabled to get very reliable results of the motion in pure solvents and also in these solvents after impurities were added. A somewhat analogous photographic method has also been used by Seddig[16] in his experiments on the influence of temperature on the Brownian movement.

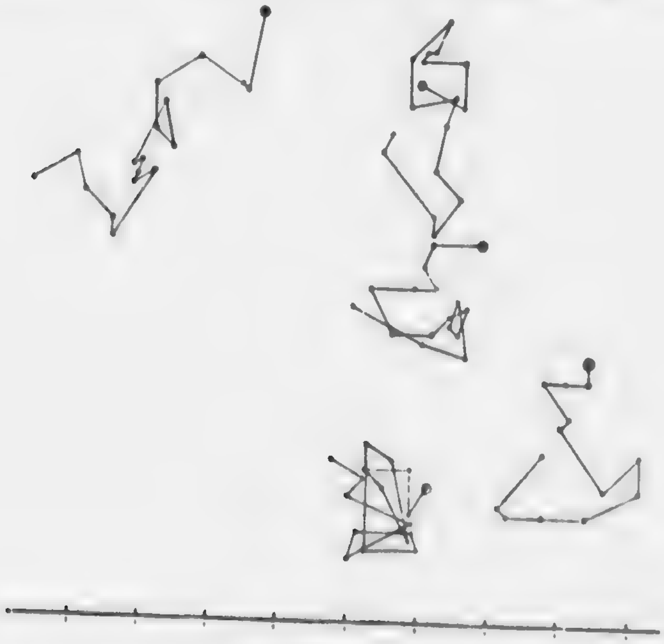

Fig. 7.

Perrin, assisted by two of his colleagues, Chaudesaigues[17] and Dabrowski,[18] applied a new method of direct observation; they marked on squared paper according to scale the position of a given particle at intervals of thirty seconds, tracing one particle for periods of twenty or thirty minutes.

Svedberg[14] followed a somewhat unique course in observing the motion. A glance at Fig. 7 (V. Henri) and

Fig. 8 (Perrin) shows that a particle oscillates in a haphazard fashion about a mean position during a short interval of time. Svedberg, by keeping a slow current of the colloidal solution passing through the cell in which he was observing the particles, gave to all the particles a slow velocity of translation in parallel straight lines across the field of view. The

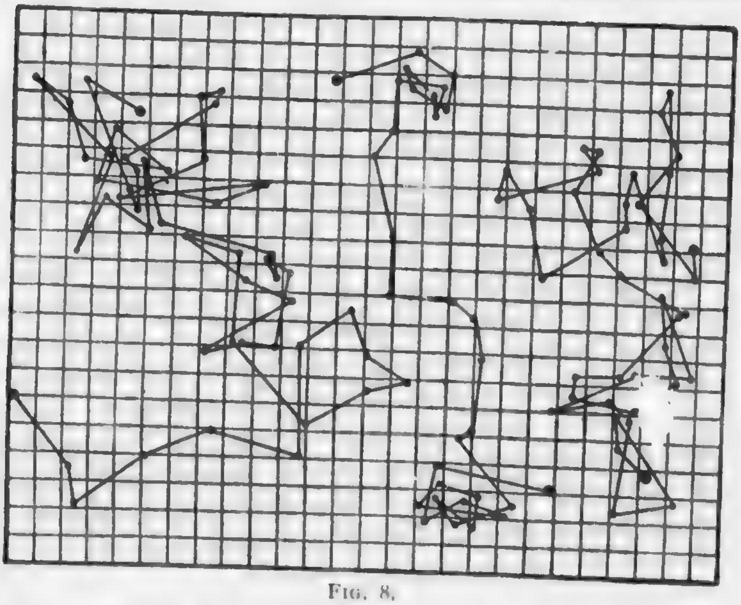

FIG. 8.

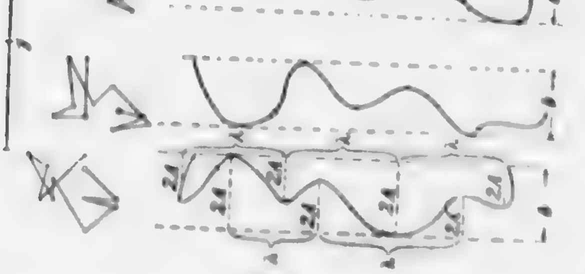

FIG. 9

effect of this motion is to give the impression that the particle is describing a wavy line—so that Svedberg speaks of the amplitude (A) and wave-length (λ) of the particle. Fig. 9 (Svedberg) shows the appearance that V. Henri[19] would have observed if he had introduced Svedberg's constant velocity of translation. The time interval between the points on Henri's figure is 1/20th of a second, and consequently each of Svedberg's composite curves corresponds to 1/2 second of time. Knowing the time, *t*, required for the impressed velocity to carry the particles the distance λ, then the mean absolute velocity of the particle would be $4A/t$.

In Table VIII are arranged all the available results giving the velocity, material, and the diameter of the particle examined, the medium, its temperature, the observer, and the method.

TABLE VIII.—BROWNIAN MOVEMENT VELOCITIES.

Observer.	Material.	Diameter $\times 10^5$ cms.	Medium.	Temperature.	Velocity $\times 10^5$cms./sec.	Method
Wiener[4]	Quartz, Gamboge, Salicic Acid, White Lead.	10·0	Water.	18°	23·0	Micrometer.
		16·0	,,	18	5·0	
Exner[5]	Sulphur, Mastic, Mica, Cinnabar, Gamboge, Charcoal.	4·0	,,	21	38·0	Scale and Watch.
		9·0	,,	21	33·0	
		9·0	,,	71	51·0	
		13·0	,,	21	27·0	
Ramsay[7]		40·0	,,	21	No motion	
Zsigmondy[10]		14·0	,,		14·0	
	Gold.	0·06	,,	20 (?)	† 700·0	
	,,	0·1	,,	,,	† 280·0	Estimated with the eye.
	,,	0·35	,,	,,	† 200·0	
	Dust particles.	2·0	,,		No motion	
Svedberg[14]	Platinum.	0·4 to 0·5	Aceton	18	3900·0	From wave-form under impressed velocity.
	,,		Ethylacetate	19	2800·0	
	,,		Amylacetate	18	2200·0	
	,,		n-Pro. Alco.	20	2900·0	
	,,		Water.	20	3200·0	
Henri[18]	Rubber Emulsion.	10·0	Water.	17	124·0	Cinematograph Observations made on single particles at intervals of 30 secs.
Chaudesaigues	Gamboge.	4·5	,,	20	† 2·4	
	,,	2·13	,,	20	† 3·4	
	,,	2·13	Sugar Sol'n.	*	† 3·1	
	,,	2·13	,,	*	† 1·5	
Perrin and Dabrowski[19]	Mastic.	10·00	Water.	20 (?)	1·55	

† These results calculated from rather indefinite data.
* Viscosity of first solution 1·2 times that of water at same temperature.
Viscosity of the second solution 4·0 times that of water at the same temperature.

Care must be exercised in comparing results such as we have in the above table, for the velocity found in any particular case depends on the time interval which elapses between two observations of the same particle. A glance at Figs. 7 and 8 will show that, as a result of the zig-zag motion, a particle may after a comparatively long interval return very nearly to its original position. In dealing with the verification of the kinetic theory formula, Smoluchowski[29] says: "Let us imagine that we could make two series of cinematographic pictures of a given particle, one corresponding to intervals of one second and the other to intervals of 1/10th of a second. The velocity calculated from the second series would be $\sqrt{10}$ times greater than that from the first series. This is probably why Exner, who used a very highly perfected method, obtained results about twice as great as those by Wiener."

4. SUGGESTED CAUSES OF THE BROWNIAN MOVEMENT.

As is shown by the quoted summary of Brown's work, the question uppermost in his mind was the cause of the motions which he observed; the same quest has engaged all the workers on this phenomenon up to the present. As a result of the work of Brown and his successors we may discard a number of theories which have been suggested. While the whole mechanism of this movement is by no means clear, we believe that the shocks of the molecules of the liquid medium are the main cause; still it is hard to imagine that the particles are not affected by such factors as surface tension and electrical forces. Before dealing with the treatment from the point of view of the kinetic theory, we may enumerate the other theories, some of which have been definitely discarded.

1. *The motion is not due to infusoria.*—This proposition differentiates the experiments of Brown from those of his predecessors: he found that the motion exists with such inanimate objects as resins, glass, rocks, and various metals. This point is also dwelt on by Wiener who observed the motion in particles of finely divided quartz after it had been heated to a temperature sufficiently high to destroy all life.

2. *The motion is not due to such external agencies as mechanical vibrations from surrounding bodies, or incident light and heat.*—Wiener, Exner, and Gouy all record experiments which show that the motion is not due to mechanical vibrations. The first named observed a sample of sol for twelve days but was unable to detect any change in the motion, while Gouy placed a sample in a cellar completely free from vibration and still found no change. It is doubtful whether the effect of external vibrations would have even a secondary effect on the particles of a drop of liquid such as was usually examined under the microscope. Wiener believed the motion was caused primarily by the light and heat waves passing through the medium, because the particles which he examined were of dimensions about the same as the wave-length of the red light of the spectrum. On examining further into this phase of the question, Exner found that the motion was affected to some extent by the incident light and heat but not sufficiently to account for the whole motion. For example, using sunlight, first with the heat rays shut off by a liquid cell, and secondly with the heat rays allowed to pass freely, the ratio of the rates of motion of the particles was 8·25 : 11·5. Exner showed that this difference was due merely to a change of temperature of the medium, as the velocity of any particle at a given temperature above the initial temperature was the same whether the heat was conveyed to the liquid by conduction or by radiation. Taking Exner's numbers for the velocities of certain particles at 20° and 71°, the difference may be completely accounted for by the change in the viscosity of the liquid. Gouy maintained a sample of sol in a constant temperature bath without noticing any change, showing that the motion is not due to temperature changes. Exner, Gouy, and Meade Bache each exposed samples to light of various wave-lengths and intensities and found little or no change in the movement; Bache kept a sample in the dark for a long period and still the motion persisted. Zsigmondy arranged the light cone so that it could be moved quickly from one region of the liquid to another but found the motion just as lively in one place as in the other

3. *The motion is not due to convection currents or to disturbances induced by evaporation of the liquid.*—Regarding the former of these two causes, Exner points out that the motion of neighbouring particles is not what would be expected if they were moved along by convection currents; even the motion of two neighbouring particles appears to be utterly haphazard. Varying the intensity of the heat rays allowed to fall upon the solution does not give any startling change in the motion, and Gouy found that the motion persists even under constant temperature conditions. Under a uniform temperature of 4° C., at which point the convection currents in an aqueous solution should be at a minimum, Bache found very little difference in the motion. Gouy also points out that in such a small space as that in a droplet 1/10 of a mm. in depth the convection currents should be enormously reduced: still the motion is apparently independent of the volume of liquid under examination.

To show that evaporation has no effect on the motion, Brown shook up some of an aqueous solution in oil so as to obtain, distributed through an oily medium, small drops of water containing the fine particles; although evaporation was thus prevented, the particles in the aqueous drops possessed the customary motion. By preventing the evaporation of the liquid under examination by hermetically sealing it, this possible cause was shown by Wiener, Bache, and Cantoni, to have no effect. Cantoni observed one sealed sample at intervals during a whole year but was unable to observe any change. Evaporation promoted artificially was shown by Wiener to have no effect.

With the causes enumerated above, we eliminate all effects which have to do with the liquid as a whole, and are now confined to the consideration of the mutual actions of the particles themselves, and the more intimate relation between the particles and the molecules of the liquid medium.

4. *Influence of the gases absorbed by the particles.*—It is a phenomenon of common observation by mineralogists that the small bubbles of gas contained in liquids enclosed in spaces in certain minerals, are in constant motion. Gouy[6] quotes

from de Lapparent's "Traité de Geologie," p. 549, as follows: "The mobile bubbles, or libelles, are the distinctive characteristics of the 'inclusions liquides' . . . ; whenever the dimensions of the libelles are below 0·002 mm., we observe that they are subject to a constant quivering motion, quite analogous to the motion of corpuscles known as the Brownian movement. The quivering of the libelles appears to be completely independent of external circumstances, such as the rigidity of the supports and temperature variations." The explanation, given by Carbonnelli and Thirion,[21] for the motion of these libelles, is founded on a supposed incessant interchange between the molecules of vapour in the libelle and those of the liquid surrounding the libelle. Maltézos[11] imagined an analogous cause for the Brownian movement of solid particles—an incessant interchange between the gaseous molecules dissolved in the liquid medium and those of the air imprisoned in small pores in the surface of the solid particles: or, again, continual evaporation of the surrounding water into these small imprisoned air-bubbles and condensation of the vapour molecules into liquid. However, Maltézos disproved this himself because, after boiling a solution for an hour to drive off the gases, sealing it, and then allowing it to cool, not in contact with the air, he found the motion as lively as ever.

5. *Influence of gravitational, electrical, and magnetic forces between the particles.*—The decision with regard to these mutual actions of the particles depends to a great extent on their apparent motions in respect to each other. Wiener concluded that the collisions of one particle with others could have little effect because diluting the solution made no change in the motion. However, Zsigmondy says "that the particles appear to influence each other and that for the most part the activity of the motion of gold particles is somewhat decreased by the dilution of the gold solution". Ramsay believed that the particles did not influence one another. Direct observation will justify the conclusion that the motion is not fundamentally due to the collision of the particles. The appearance is very much in accordance with Spring's suggestion, viz.: "It is to be remarked that when two droplets (of gamboge emul-

sion) collide they rebound without coming into contact; there must be, then, surrounding each droplet, an adherent liquid layer which prevents contact at the moment of collision".

That the cause of the motion lies in the electrical forces acting between the particles was first suggested to Jevons by the influence of electrolytes in producing the coagulation of these solutions. The Brownian movement always exists when particles are in suspension, and since, as Jevons thought, only electrolytes produced a cessation of the movement and consequent coagulation, electrolytes must have some electrical effect in stopping the motion, and, therefore, the motion must be due primarily to electrical forces between the particles. It has been found almost invariably that the addition of electrolytes stops the Brownian movement. The truth of this statement is asserted by Jevons, Gouy, Ramsay, Maltézos, Bliss,[22] Spring, Zsigmondy, Henri, and others; these men worked with a large variety of colloidal solutions and tried the influence of both electrolytes and non-electrolytes. Jevons mentions that sodium silicate increases the movement, ammonia or boracic acid does not affect the motion or cause coagulation, while acetic acid produces precipitation although it is a weak electrolyte. Testing cinematographically the action of various substances on rubber emulsion, Henri found that the Brownian movement is retarded by the addition of a coagulative reagent before the phenomena of coagulation appear; acetic acid, which has an especially keen coagulant effect on this rubber emulsion, produced retardation before coagulation; alcohol acts similarly; the addition of urea, which does not coagulate the solution, has no effect on the motion of the particles. Bliss records that the addition of extremely small traces of alkalies to suspensions of clay and finely divided sand accelerates the Brownian movement, but with increasing doses the movement is retarded: the addition of acids and neutral salts always causes flocculation. Maltézos holds that we get different appearances under different circumstances; in some cases the particles unite to form large masses and the Brownian movement ceases at once, while in other cases the particles increase in size slightly and the motion persists. Svedberg alone maintains that the Brownian movement is independent of the electrical charge. In his method of impressing a velocity on the particles, he found that the amplitude of a silver particle was independent of the direction of its cataphoresis, which can be changed by the addition of salts, e.g. aluminium sulphate.

According to Smoluchowski[23] electrical forces between the particles " would be able to produce a certain grouping of the particles, but not a continuous motion ". While this objection would hold for a system of particles held in a state of equilibrium, it seems hardly justifiable when applied to a liquid medium, because there always would be influences at work tending to disturb the particles, so that the system would be striving towards, but never attaining to, an equilibrium state of rest. At any rate, the motion resulting from such a state of affairs would show a much more intimate interaction between the suspended particles than is apparent to the eye.

It seems justifiable in view of all the evidence to assume that the charge on the particle exerts some influence in keeping the particles in a finely divided state, while it is probably only rarely that the electrical forces can intervene to alter the motion of the particle. The cessation of the Brownian movement, when it takes place, is due not to the addition of impurity to the liquid, *per se*, but merely to the impossibility of the forces at play making a visible effect on the large masses produced in flocculation. In the process of flocculation the particles coalesce gradually and, if the growth is not too rapid, the alteration in the Brownian movement may be apparent, as in Henri's results.

Under the belief that electrical forces might be the cause of the motion, Gouy[6] and Bache[24] examined the effect when the solution under observation was exposed to a strong magnetic field but they found no change. Of course this does not apply to the action of a magnetic field on various iron solutions (see Cotton and Mouton[25]).

6. *The influence of surface tension.*—In the production of the Brownian movement there is experimental evidence of several contributing causes, each bearing its part in the action.

While the majority of the workers, from Brown onward, have hinted that the cause lies in the molecular motions in the liquids, there have been other suggestions strongly supported, as, e.g., electrical forces (Jevons) and surface tension (Maltézos). I know of no valid reason for maintaining that these two forces have not a very intimate relation to the Brownian movement: on the other hand, there appears to be insurmountable difficulty in proving that these forces, either alone or combined, would cause the motion.

One undisputed property of the Brownian movement is that, for a given solution, the motion varies inversely as the size of the particles; 4 μ seems to be the maximum diameter of a particle showing the motion. There are really two conditions for the maintenance of the Brownian movement: in the first place, the particles must be kept less than a certain size in order to have a motion visible to us, and in order to keep the suspended matter from sinking to the bottom of the containing vessel; in the second place, the particles must be made to move. Taking the experiments as a whole, we may ascribe the regulation of the size of the particle to surface tension effects, influenced, as they must be, by the electrical charges on the particles; and to the kinetic theory we must look for the explanation of the motive power necessary to give the particles their curious random paths.

The rôle of surface tension in deciding whether small particles will unite to form larger ones or still further subdivide, is definitely laid down in two laws stated by Fucks[26]:—

(1) If the molecules of the liquid are attracted more strongly by those of the solid than they are by neighbouring molecules of the liquid or than the molecules of the solid attract one another, the potential energy will be a minimum when each particle of solid is surrounded by a shell of liquid of thickness equal to the radius of molecular forces. The two particles will then repel each other if brought closer together than twice this distance.

(2) If either of the forces, solid-solid or liquid-liquid, is greater than the force solid-liquid, the potential energy will be

least when the two particles are made to approach as closely as possible. They will then attract each other.

Such facts as these are undoubtedly of importance in regulating the size of the particles.

We have unmistakable evidence in the work of Jevons, Maltézos, Bliss, and Henri, that certain substances added to colloidal solutions have the effect of producing finer subdivision of the suspended particles and more rapid Brownian movement. The influence of the electrical charge relative to the surface tension has been developed by Bredig,[27] and it is quite apparent that we have here tremendous forces capable of altering the sizes of the particles. On the other hand, to establish the proposition that the motion is caused by surface tension, leads to hypotheses so artificial as to be untenable. In attempting to do this, Maltézos sums up the forces acting on the particles as follows: "We have then the excess of the weight of the particle (over that of an equal volume of the liquid), the hydrodynamic forces and the forces of internal friction of the liquid: these two latter do not remain invariable during the continuance of the motion inasmuch as they depend on the velocity and the surface of the particle. (These forces all tend to retard the Brownian movement.) The surface tension (between the particle and liquid) being the same all around the particle, its effect will be zero, except in one of the following cases: (1) when there are traces of foreign matter about the particle; (2) when there are pores in the surface filled with gas, or with the vapour of the liquid; (3) if near the particle the liquid is not pure." In a later paper Maltézos pins his faith to the last of these conditions. Mensbrugghe[28] suggests a similar explanation from the supposed analogy of the action of small pieces of camphor on the surface of water. However, as Smoluchowski[23] points out, any explanation which postulates the existence of the unequal distribution of impurities, assumes tacitly that a state of equilibrium should be reached eventually, at which time the motion would cease. This explanation is consequently put out of court by the unchangeableness of the movements observed throughout long intervals of time.

5. THE KINETIC THEORY OF THE BROWNIAN MOVEMENT.

1. *Development of the theoretical formula.*—Although nearl every observer of the Brownian movement has ascribed it to molecular action of the liquid, it is only of recent years this theory of the motion has been given mathematical fo Smoluchowski,[23] Einstein,[29] and Langevin [30] have attacked the problem by independent avenues and have been led to practically the same formula, which gives the relation between the distance moved by a particle in a certain time, the radius of the particle, the temperature and viscosity of the liquid, and the time of observation.

A kinetic theory of this motion was first stated definitely by Wiener,[4] and Exner,[5] and later by Clausius. Afterwards Gouy [6] wrote "the Brownian movement, of all physical phenomena, shows us visibly that there is a constant state of internal agitation in liquids, even in the absence of all external causes" —a statement by which he replaces the dictum of Maxwell that "under the most powerful microscopes bodies show the most perfect repose". Maltézos [11] quotes from a lecture by Boussinesq: "The whole of a liquid is at a certain definite temperature and not at absolute zero. It is necessary that the thermal agitation should reach a given value in order that the bodies may become liquid, when the molecular vibrations shall have reached an amplitude sufficient to disengage the molecules from one another. It is probable that the movement called Brownian is due to this thermal motion of the molecules" Regarding the same question Zsigmondy [10] wrote: "Although the causes of this remarkable phenomenon may be manifold, it is the kinetic theory of fluids which appears to be of prime importance in explaining the motion, which persists uninterruptedly in the fluid for months and years".

In treating of the development of the kinetic theory of this motion one could not do better than adopt the language of Smoluchowski who gives the following direct treatment of this phase of the subject

"The direct observation of this movement, by means of the microscope, produces an impression analogous to our imagination of molecular motions. It is not a vibration, nor a simple progressive movement, but it is rather a trembling, or, as Gouy expresses it, a swarming. The particles pursue an irregular zig-zag course, in all directions in space, as if they were pushed here and there by accidental collisions with the molecules. In reality their progress is very slow in spite of their feverish activity. Many physicists have considered this phenomenon as a visible proof of the truth of the kinetic theory. . . .

"We shall study here the simplest kinetic theory; we shall assume that what we see in this motion is the result of accidental collisions between the particles and the molecules of the liquid. One objection often considered as fatal to this theory was first raised by Nageli. He shows that the velocity transmitted to a spherical particle of diameter 0·003 mm. by collision with one molecule of hydrogen is only 2×10^{-6} mm. per second, which would not be visible in the microscope; in addition, the shocks received on the various sides of the particle would annul each other and give no perceptible result.

"This conclusion is comparable to that error which one makes who pursues a game of chance, if he expects never to have a loss or a gain more than the simple wager. One knows that, in general, the chances do not balance exactly and that the amount of the sum lost or gained increases with the number of plays. We have in the problem before us to discuss the excess in the number of shocks given to a particle by the molecules in a certain direction. Now we have the simple result that the velocity transmitted to a particle of mass, M, in repose, by a direct collision with a molecule of mass, *m*, which is moving with a velocity, *c*. will be: $C = mc/M$ which is of the order given by Nageli: and further the absolute value along a fixed direction, X, will be still smaller. But it is necessary to consider that the particle M suffers more than 10^{14} collisions per second in a gas and more than 10^{20} in a liquid, of which the effect will be annulled in general: but there will always be an excess, + or −, of 10^{8} or 10^{10} collisions, by virtue of which the particle will attain a velocity of from 10 to 1000 cms. per second in the direction of X (+ or −).

"This proves that the objection of Nageli is not justified, but the final result, on the other hand, is not exact. For (*a*) the absolute value of the change in the velocity of M will not be the same for each collision, but will depend on the absolute value of C at the time, and (*b*) the probability of collisions retarding will be greater than that of collisions accelerating for large values of C. These two factors oppose an unlimited increase in the value of C: the final result which one can readily foretell for the kinetic theory is that the mean kinetic energy of translatory motion of M will become equal to the mean kinetic energy of the molecules. For the equalization of this value is precisely the characteristic condition of the thermal equilibrium of bodies, according to the theory of Boltzmann and Maxwell. In the same way we conclude that the particles play the rôle of highly polyatomic molecules of some dissolved substance, and that they would consequently have the same kinetic energy as a molecule of a gas at the temperature of the medium. Then one can calculate the value of C according to the ordinary formula of the gas theory

$$C = c\sqrt{m/M} \qquad . \quad . \quad . \quad . \quad (1)$$

which for a particle of diameter equal to 0·001 mm. and a density 1, gives for C, 0·4 cm. per sec. How are we to reconcile this result with the observed values, which are of the order of 3×10^{-4} cm. per sec.? This obstacle seems at first sight a serious matter for the kinetic theory. However the explanation is very simple. It would be impossible to follow the movement of such a particle if it were endowed with a velocity of 0·4 cm. per sec., for in a microscope of magnification 500 it would be moving with a velocity of 2 metres per sec.

"That which we see is the mean position of the particle, pushed 10, 20 times per second with this velocity, each time in a different direction. Its centre describes a capricious, zigzag path, composed of straight pieces each very small in comparison with the dimensions of the particle. Its displacement is visible only when the geometrical sum of its paths is raised to an appreciable value. In addition there is the minor correction that it is not the movement in space we observe but the projection of this movement on a plane, consequently, we shall have to multiply observed results by $4/\pi$."

Smoluchowski then proceeds to determine the mean distance, D_x, traversed in one second by a spherical particle of mass M under the influence of *n* collisions with molecules each of mass *m*. What he really calculates is the square root of the mean square of the distance, but, as he points out, the numerical difference is small and may be left out of consideration. There are two main cases, according as the radius, *a*, of the particle is (1) small compared with the mean free path, λ, of the molecule of the medium, or (2) large compared with the value of λ; the latter is the case in point for the Brownian movement in liquids. The rigid treatment of the first case leads to the following equation:—

$$D_x = \frac{4\sqrt{2}}{3} \cdot \frac{c}{\sqrt{n}} \quad . \quad . \quad . \quad . \quad (2)$$

where *c* is, as above, the mean velocity of the molecules of the medium. This leads to the rather surprising result that the value of D_x does not depend on the mass of the particle, but only on the nature of the medium and the number of collision per second.

The essential assumption made in deducing the above formula is that one may neglect the reaction of the movement of the sphere M on the distribution of the velocities of the neighbouring molecules. Then the collisions with M will be independent, accidental events, and the curvature of the path which M traverses will be, with equal probability, in any plane whatever, determined by the instantaneous direction of the movement of M. When we come to deal with the second case, in which *a* is comparable with λ, the shocks of the molecules against M will no longer be distributed with equal probability in all directions, since layers of the liquid contiguous to the sphere will participate in the motion—a circumstance which will have the effect of preventing abrupt changes in the direction of motion of M and, consequently, the effect of increasing the value of D_x. This circumstance led Smoluchowski to use a second method of attacking the problem—a method not so exact as the former, but simpler.

"Suppose a particle, M, launched in a medium with an initial velocity C; it will suffer retardation of movement (of the resolved part of the velocity parallel to the original direction, according to the formula

$$v = \mathrm{C} \, . \, e^{-t/\tau}$$

where τ is equal to the mass of the particle divided by the coefficient of resistance, or M/S. But the kinetic energy of the centre of gravity of the particle will not diminish if C has the value given in (1). The sphere loses its original velocity but in return gains velocity normal to that direction, so that the resultant velocity does not change.

"We may regard the time of relaxation, τ, as a measure of the continuance of rectilineal motion, and the paths τ . [illegible] MC/S, as a measure of the rectilineal path. The movement of M can then be expressed as the movement of a gaseous molecule, which travels out from its initial position in a zig-zag fashion, its path being composed of short, straight parts of length equal to the apparent mean free path

"The mean distance attained in time, t secs., by such a molecule, is given by the gas theory as

$$\mathrm{D}_x = \lambda\sqrt{nt} = \tau \, . \, \mathrm{C} \, . \, \sqrt{n \, . \, t} = \mathrm{C}\sqrt{\tau \, . \, t} = \mathrm{C} \, . \, \sqrt{\frac{\mathrm{M}}{\mathrm{S}} \, . \, t}$$

$$= c\sqrt{\frac{m}{\mathrm{S}} \, . \, t} \text{ since } \tau = \frac{1}{n} \quad . \quad (3)$$

This calculation is not exact in all points but the order of the result is true."

Applying this formula to the case of a particle moving in a rare gas and reckoning S by means of the gas theory, Smoluchowski finds that in 1 second

$$\mathrm{D}_x = c \, . \, \sqrt{\frac{3}{2n}} \quad . \quad . \quad . \quad . \quad (4$$

If this value of D is multiplied by the numerical factor $\frac{8}{3\sqrt{3}}$ we get the value given by the exact theory (2). This then may be treated as a modifying factor in a result obtained by the use of equation (3), and we have given as the general equation

$$\mathrm{D}_x = \frac{8}{3\sqrt{3}} \, . \, c \, . \, \sqrt{\frac{m}{\mathrm{S}} \, . \, t} \quad . \quad . \quad . \quad (5)$$

In the case of a small sphere moving in a liquid, we have S given by Stokes' law, viz. : S = $6\pi\eta a$. The displacement, D_x, described by M becomes

$$D_x^2 = \frac{32}{27} \cdot \frac{c^2 mt}{3\pi\eta a} . \quad . \quad . \quad . \quad (6)$$

The motion considered above is that parallel to one particular direction and, since the kinetic energy of a molecule due to its motion parallel to a given direction is RT/2N, $mc^2 =$ RT/N. Substituting in the above equation we have finally

$$D_x^2 = \frac{32}{27} \cdot \frac{R}{N} \cdot \frac{T . t}{3\pi\eta a} \quad . \quad . \quad . \quad (7)$$

Independently of Smoluchowski, Einstein[29] developed a similar formula for the motion of small spheres suspended in a liquid medium ; he applied the laws of osmotic pressure to the particles and evaluated their diffusion in the medium. The diffusion coefficient, d, of a material suspended in the form of small spheres in a liquid is given by

$$d = \frac{RT}{N} \cdot \frac{1}{6\pi\eta a} . \quad . \quad . \quad . \quad (8)$$

Again, the mean value of the displacement, D_x, of a sphere along the X-axis in time t is

$$D_x = \sqrt{2d . t} \quad . \quad . \quad . \quad . \quad (9)$$

From (8) and (9) we get :—

$$D_x^2 = \frac{R}{N} \cdot \frac{T . t}{3\pi\eta a} \quad . \quad . \quad . \quad (10)$$

This formula differs from Smoluchowski's by the dropping of the numerical factor 32/27.

More recently, Langevin[30] offered a very simple solution of the same problem, and obtained the same result as Einstein. If a particle is moving with a component velocity parallel to the axis of X equal to $\xi = dx/dt$, under the action of a force X due to molecular shocks, it will suffer a resistance given by $6\pi\eta a\xi$, according to Stokes' law. The equation of motion will then be

$$m\frac{d^2x}{dt^2} = -6\pi\eta a\frac{dx}{dt} + X.$$

The force X is varying and is indifferently positive and negative, but maintains the motion which would otherwise be stopped by the viscosity of the liquid. Multiplying through by x, the equation may be written

$$\frac{m}{2}\cdot\frac{d^2(x^2)}{dt^2} - m\xi^2 = -3\pi\eta a\frac{dx^2}{dt} + \mathrm{X}x.$$

Taking the mean of a large number of identical particles, the term in $\mathrm{X}\,.\,x$ disappears on account of the variation in X: writing $\frac{d\overline{x^2}}{dt} = z$, we obtain

$$\frac{m}{2}\cdot\frac{dz}{dt} + 3\pi\eta a z = m\xi^2.$$

Now $\frac{1}{2}m\xi^2$ is the average kinetic energy of a particle, due to the component of its velocity parallel to the axis of X. On the kinetic explanation of the Brownian movement, this energy is equal to that of a single molecule of the liquid, or to that of a gaseous molecule, parallel to a given direction.

$$\therefore\ m\xi^2 = \frac{\mathrm{RT}}{\mathrm{N}}$$

and
$$\frac{m}{2}\cdot\frac{dx}{dt} + 3\pi\eta a z = \frac{\mathrm{RT}}{\mathrm{N}}.$$

The general solution of this differential equation is

$$z = \frac{\mathrm{RT}}{\mathrm{N}}\cdot\frac{1}{3\pi\eta a} + \mathrm{C}\,.\,e^{-\frac{6\pi\eta a}{m}t}.$$

When the motion reaches a steady state

$$z = \frac{\mathrm{RT}}{3\pi\eta a\mathrm{N}}$$

from which, by integration, we get D_x from the equation

$$\mathrm{D}_x^2 = \frac{\mathrm{R}}{\mathrm{N}}\cdot\frac{\mathrm{T}t}{3\pi\eta a},$$

a result identical with that of Einstein.

As is emphasized by Smoluchowski, we should not expect very exact correspondence between this theoretical formula and observation, for, in addition to simplification of the problem mathematically, we have made two assumptions, the importance of which cannot be gauged very exactly in the case of liquids, viz.:—

(*a*) that the particles may be regarded as rigid spheres, and (*b*) that the forces of surface tension need not be considered. Nevertheless, the tests which have been made up to the present justify the formula as regards its dependence on temperature, time, viscosity, and the radii of the particles: while many of the exact determinations of the absolute values of D_x do not depart very much from the theoretical value.

(*a*) *Experimental verification of the theoretical formula.*—*a.* Observed values of D_x.

In the formula for D_x, putting N, the number of molecules in a gram molecule, equal to 7×10^{23} and $R = 83 \times 10^6$ c.g.s. units,

$$D_x^2 = 12{\cdot}6 \times 10^{-18} \cdot \frac{T \cdot t}{\eta \cdot a}.$$

In Table IX are arranged the calculated and observed values of D_x, from some of the data given in Table VIII.

TABLE IX.—CALCULATED AND OBSERVED VALUES OF D_x.
($D_x = 12{\cdot}6 \times 10^{-18} \cdot Tt/\eta a$.)

Name of Experimenter.	Radius in cms. × 10^{+8}	Viscosity.	Temp. Cent.	D_x (calculated) in cms./sec. × 10^{+8}	D_x (observed) in cms./sec. × 10^{+8}
Wiener[4]	5·0	·0107	18	8·2	23·0
"	8·0	·0107	18	6·5	5·0
Exner[8]	2·0	·01	21	13·6	38·0
"	4·5	·01	21	9·0	33·0
"	4·5	·004	71	14·3	51·0
"	6·5	·01	21	7·5	27·0
Zsigmondy[10]	·05	·01 (?)	20 (?)	227·5	280·0
Henri[18, 19]	5·0	·011	17	36·0	124·0
Chaudesaigues[17]	2·13	·01 (?)	20 (?)	*3·4	*3·6
Perrin and Dabrowski[18]	5·00	·01 (?)	20 (?)	1·56	1·55

In the above calculations the values for *t*, the interval during which the displacement was observed, were as follows: 1 sec. for Wiener and Exner, 1/7 sec. for Zsigmondy, 1/20 sec. for Henri, and 30 secs. for Chaudesaigues. It has been pointed out already that the value of the velocity in cms. per sec. depends on the interval of time through which the particle is observed. If D_x is the distance traversed in time *t*, then the velocity, *v*, in cms. per sec. will be D_x/t: therefore, under given constant conditions, $v^2 \cdot t =$ a constant; i.e. the smaller *t*, the larger will be *v*.

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* These results were calculated from Chaudesaigues' statement that his results satisfy Einstein's formula with the value $6{\cdot}4 \times 10^{23}$ for N, and from a similar statement by Perrin.

Svedberg's[14] confirmation of the formula was carried out with platinum particles in various liquid media, by observations using a value of *t* of the order of 2 or 3 one-hundredths of a second. In Table X are arranged the values taken from Svedberg's paper.

TABLE X.—SVEDBERG'S RESULTS FOR PLATINUM PARTICLES.

Medium.	Radius in cms. × 10^5	Temp. Cent.	Time, *t* in secs.	Viscosity.	D_x in cms. × 10^5	Velocity cms./sec. × 10^5 (calcul.).	Velocity in cms./sec × 10^5 (observed).
Aceton	0·25	18	0·032	·0023	14·2	444	3900
Ethylacetate	0·25	19	0·028	·0046	9·4	336	2800
Amylacetate	0·25	18	0·026	·0059	8·0	308	2200
Water	0·25	20	0·013	·0102	4·3	324	3200
Propyl alcohol	0·25	20	0·0009	·0226	2·4	266	2900

In order that a reliable comparison may be made with the results of Table IX, the velocities in Table X have been expressed in cms. per sec. and the same value of N has been used as that in working out Table IX. (Svedberg took N equal to 4×10^{23}.)

The only conclusion that we can draw from these results is that the order of the displacements given by Einstein's formula is correct. Smoluchowski's formula gives results a little more in conformity with the observed facts than that of Einstein.

(*b*) *The influence of the viscosity of the medium and the temperature.*—Referring to the outline of Svedberg's method of observation, given on page 58 and in Fig. 9, if we put in Einstein's formula, D = 4A, *t* will be the time required for the particle to make one complete oscillation. Therefore we have

$$(4A)^2 = \frac{RT}{N} \cdot \frac{1}{3\pi a} \cdot \frac{t}{\eta}$$

Now, if we treat of the same sized particles in various liquids at the same temperature,

$$A^2 = k \cdot \frac{t}{\eta}.$$

where *k* is a constant

Since, by this kinetic theory, the average kinetic energy of a particle is the same as the average kinetic energy of a molecule, and since the molecules of all fluids at the same temperature have the same average kinetic energy, we should expect the average velocity of all the particles to be the same, provided their masses are the same, whatever the liquid in which they may be moving. Svedberg remarks that the numbers in the last column of the above table may be taken as sensibly constant and, therefore, Einstein's formula demands that the product $\eta . a$ should also be constant. Svedberg gives the curve, Fig. 10, showing the relation between the numbers in the fifth and sixth columns, from which we see that the demand of the formula is practically met.

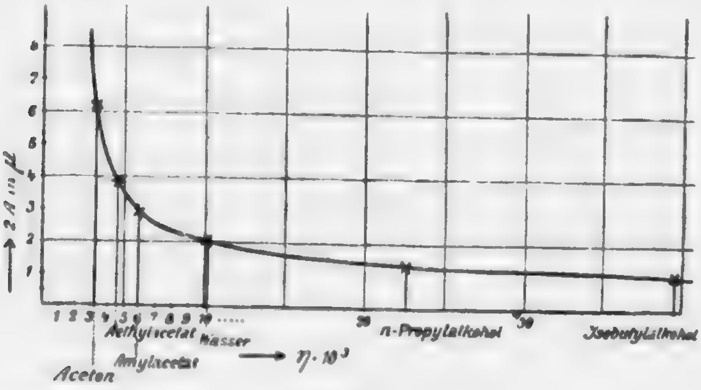

FIG. 10.

Results of measurements made at temperatures of 20° C. and 71° C. are given by Exner and will be found in Table IX: the ratio of the values of D_1 in these two cases is 1 : 1·6, while the ratio of the corresponding values of $\sqrt{T/\eta}$ (for water) at these two temperatures is 1 : 1·7.

Seddig[16] has shown by means of a photographic method in conjunction with the microscope, that finely divided cinnabar in water obeys Einstein's formula, the greatest departure from the theoretical value being 6 per cent; as is the case with nearly all the results, the observed velocity exceeds the calculated. Seddig changed the temperature over a long range but found that the value of $\sqrt{T/\eta}$ was practically constant.

Chaudesaigues,[17] working with an emulsion of gamboge varied the viscosity of a solution by adding sugar. In this way he carried out observations on two solutions containing the same sized particles at the same temperature, the viscosities of which were in the ratio of 1 : 4 and found that the motion was twice as fast in the less viscous solution as it was in the solution of higher viscosity.

(*c*) *Relation of the radius of the particles.*—Table IX shows that the velocities observed are greater for the small particles than for the large ones. Chaudesaigues also tested this point by observing the velocities of particles of gamboge with radii respectively $4{\cdot}5 \times 10^{-5}$ cm. and $2{\cdot}13 \times 10^{-5}$, practically a ratio of 2 : 1, and found that these velocities varied inversely as the square of the radii. (This result may be calculated from Table IX.)

(*d*) *Relation of the time interval, t.*—We are indebted to Chaudesaigues[17] also for a direct test of this point. He observed the distances described by 50 grains, each of diameter $2{\cdot}13 \times 10^{-5}$ cm. during successive intervals of 30 secs. each and obtained the following results: the particles moved over on the average

6·7, 9·3, 11·8, and 13·95 microns in
30, 60, 90, and 120 seconds. The square roots of the times are proportional to the numbers,

6·7, 9·46, 11·6, and 13·4, giving an ideal confirmation of this point.

(*e*) *The velocity independent of the material and mass of the particle.* —This brings up a debatable question. Gouy[6] and Jevons[3] maintain that the motion is independent of these two circumstances, while Cantoni[8] and Ramsay[7] hold that the motion depends on the material and density of the particle. Physically, Smoluchowski explains the motion being independent of the mass by the fact that the smaller velocity which would be communicated to the particle of larger mass, M, would be counterbalanced by a greater persistency of velocity possessed by the larger particle once it is moving. When it is borne in mind that the theory deals with the particles as if they were rigid spheres, and that in reality this cannot be realized, we may expect the motion to depend to some extent on the material of the particle; consequently we need not bring the essential truth of the theory into doubt if we do find that the material of the particle affects the movement. In fact, Zsigmondy states that the "nature of the subdivided substance appears to influence the motion: for example, the ultra-microscopic dust particles of distilled water do not show an appreciable motion".

(*f*) *The Brownian motion of rotation.*—Considering the rotations which should be produced in the particles by the molecular shocks, as well as the translation, the energy of rotation of a particle will be, on the average, equal to its mean energy of translation. Einstein obtained the following equation for the mean square of the angle of rotation, d, in a time, t, relatively to an arbitrary axis:—

$$d^2 = \frac{RT}{N} \cdot \frac{t}{4\pi\eta a^3}.$$

Perrin[31] has made this test of the theory by observing the time of rotation of comparatively large grains of mastic (diameter 13μ). These particles could be seen in the ordinary microscope and the time of rotation was noted by the periodic appearance of certain defects in the surfaces of the particles. The difficulty of coagulation was overcome by suspending the particles in a solution of urea of the same density as the particles. The results of substituting observed values of σ, η, a and t in the above formula gave a value of N equal to $6{\cdot}5 \times 10^{23}$, which confirms the theory.

After the foregoing rather rigorous comparison of theory and observation, we are justified in regarding the Brownian movement, in the words of Smoluchowski, "as a visible proof of the reality of our molecular and kinetic hypotheses. If we reduce the Brownian movements to a kinetic phenomenon, we have no longer to inquire for the source of the energy of the motion, since the energy dissipated by viscosity has its origin in the energy of the heat motion. Gouy remarked that this motion would be a contradiction of Carnot's principle, if one were able to concentrate the mechanical effects of the movements of the particles. In effect this would be a way of

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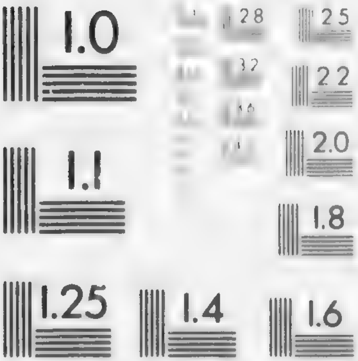

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transforming heat into work, which is not practical on account of the grossness of our instruments; but it is more interesting in that it does not seem as impossible as the pursuit of the molecules by the aid of Maxwell's demons." [23]

6. PERRIN'S TEST OF THE KINETIC THEORY OF THE BROWNIAN MOVEMENT

(*a*) *Perrin's law of the concentration of particles at different heights.*—One of the most remarkable contributions to the kinetic theory of the Brownian movement has been made by Perrin [32] and his collaborators.

If one could obtain a uniform dispersoid of any material, i.e. one in which the granules are identical in size and in shape, these granules should arrange themselves in the liquid at rest according to the same law that is obeyed by the molecules of a gas under the action of gravity. For the same reason that the air is more dense at sea level than at the tops of mountains, the granules of the emulsion, whatever may have been their initial distribution, will reach a steady state in which the concentration will diminish as a function of the height from the lowest layer; and indeed the law of rarefaction will be the same.

Suppose we have a uniform emulsion in equilibrium in a vertical cylinder of cross-section s. The state of a thin section of the liquid comprised between the levels h and $h + dh$ would not be changed if the section be enclosed between two pistons permeable to the water molecules but impermeable to the granules themselves. On each of these pistons there would be an osmotic pressure due to the bombardment by the granules which they enclose. If the emulsion is dilute, this osmotic pressure may be calculated in a manner similar to that employed in the case of dilute solutions, according to which, if at a height h there are n grains per unit volume, the osmotic pressure, P, will be $2/3 . n$ W, where W equals the mean kinetic energy of a granule. Similarly at a height $h + dh$ the value of the osmotic pressure will be $2/3\,(n + dn)$ W. Now since the granules in the section do not fall, there must be equilibrium between all the forces acting on them, viz. (1)

the difference in the osmotic pressures at h and $h + dh$, (2) the total weight of the granules, and (3) the buoyant force due to the liquid.

If v = the volume of each granule,
u = the density of the granule,
w = the density of the intergranular liquid,

the above conditions of equilibrium give us the following equation :—

$$-\tfrac{2}{3} . s . W . dn = n . s . dh . v(u-w) g.$$

Integrating from height zero to height h, we find :—

$$\tfrac{2}{3} W . \log \frac{n_0}{n} = \frac{4}{3} . \pi a^3 . (u-w) gh,$$

where n_0 and n are the initial and final values of n, and a is the radius of the particles. This equation shows that the concentration of the granules of a uniform emulsion should decrease in an exponential fashion as a function of the height or, in other words, if the heights increase in arithmetical progression, the rate of distribution of the granules should decrease in geometrical progression: this is true, of course, provided that W may be treated as a constant with regard to n and h.

Perrin tested the truth of this equation by measuring each of the quantities, u, a, and n_0/n for certain values of h, using solutions of gamboge and mastic prepared by methods already recorded.

a) *Determination of the density of the particles.*—The density was determined in two ways, both of which depend on the fact that one can find the weight of solid substance in a given sample of solution, by evaporating the latter and weighing the dry residue

The first method was simply to find the specific gravity of the dried vitreous mass in the ordinary way.

In the second method the weights of water and of the emulsion required to fill a specific gravity bottle were found first; then the emulsion was evaporated and the weight of solid in the given weight of emulsion obtained

If m = the weight of water filling the bottle,
m' = the weight of emulsion filling the bottle,
m'' = the weight of solid in weight m' of emulsion,
d = density of the water,

$$\left\{\frac{m}{d} - \frac{m - m''}{d}\right\} = \text{volume of the solid in weight } m' \text{ of solution.}$$

Therefore, the density of the solid is

$$\frac{m''}{\left\{\frac{m}{d} - \frac{m' - m''}{d}\right\}}.$$

These two methods gave concordant results—0·207 for the apparent density of gamboge, and 0·063 for that of mastic.

(b) *Measurement of the radii of the particles.*—Three methods which gave results agreeing well among themselves were used in this determination.

First the rate of fall of the upper surface of the cloud of particles in a solution enclosed in a vertical capillary tube, and kept at a constant temperature, was measured and the radius determined from Stokes' law.

As a second method, Perrin counted the number of particles in a given volume of emulsion: he noticed that in a slightly acidulated solution the granules of gamboge become fixed to the glass walls when they approach near enough. After some hours the granules in a small volume viewed in a microscope stick to the wall and can then be counted.

In the third place it was noticed that, in a slightly acidulated solution, the particles sometimes stick together in a string, which becomes attached to the wall: the length of this string of particles was measured and the number in it counted, from which the diameter could be deduced.

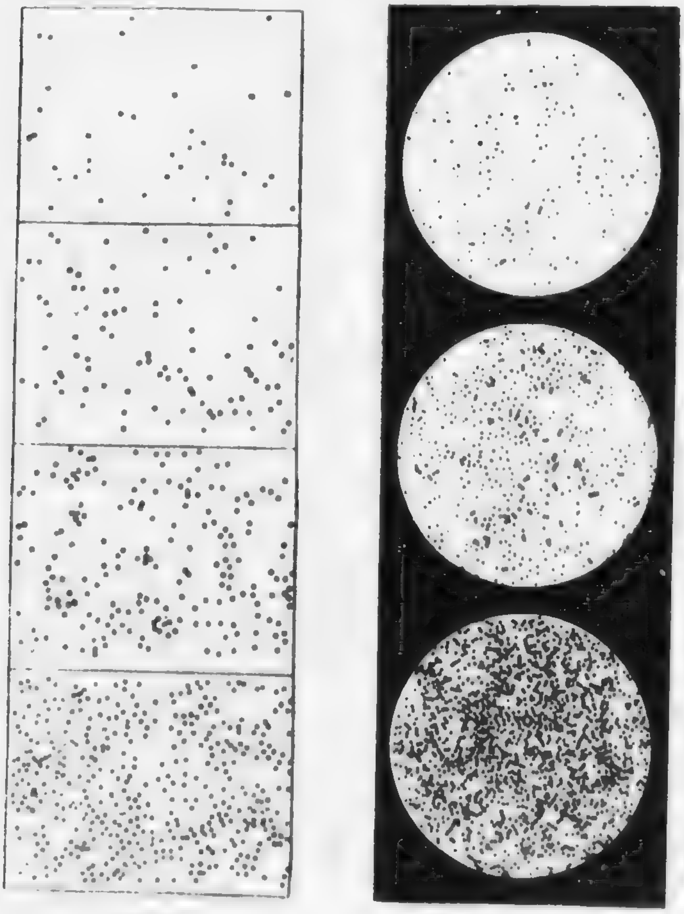
Variously sized particles, from 0·52 μ to 0·14 μ in diameter, were measured by these means. In one case the three methods gave for the same particles, 0·45 μ, 0·46 μ, and 0·455 μ, respectively; as a second example, the application of Stokes' law to a certain solution gave a diameter equal to 0·213 μ, while counting 11,000 granules in the second method gave 0·212 μ.

Perrin uses the concordance of these results to support the hypothesis that the laws of internal friction established for the displacements of large objects in a uniform fluid, apply to the displacements of small objects which show the Brownian movement. This is a very important point as Stokes' law is used by Einstein, Smoluchowski, and Langevin in the deduction of the formula for D_x^2.

(*c*) ***Relation between*** n_0/n ***and*** h.—In obtaining this relation Perrin viewed a cylindrical column of height 1/10 mm. under a microscope, which could be focussed at different heights in the liquid by turning the micrometer screw. When the liquid is first put in the apparatus the distribution of the particles is apparently uniform, but in a few minutes it is quite evident that in the lower layers the particles become more closely packed than in the upper layers. The distribution reaches a steady state, and the particles all remain in suspension; Perrin found that the arrangement was the same at the end of fifteen days as at the end of three hours.

As an example of his results, Perrin gives his most careful observations, made on granules of gamboge of diameter 0·212 μ. The numbers of particles visible at heights differing by 30 μ were counted; in all some 13,000 particles were observed in this one experiment. The following values of h : 5 μ, 35 μ, 65 μ, 95 μ, gave concentrations proportional to : 100, 47, 22·6, 12. These numbers differ very little from : 96, 48, 24, 12, which are in geometrical progression. The coincidence is striking enough to confirm the above formula. Perrin tested this law for granules of gamboge of various sizes and, assisted by Dabrowski, for particles of mastic of density 1·063, and satisfied himself of the truth of the formula. In Fig. 11 (Perrin) are drawings of the distribution of the particles in gamboge (gomme-gutte) and mastic; in the former, the levels taken were at intervals of 10 μ with particles 0·6 μ in diameter, while in the case of the mastic, the intervals were each 12 μ and the diameters 1 μ. It is interesting to note that the concentration drops to half value in about ·03 mm difference of level, whereas in the atmosphere the same proportional decrease requires a difference of level of 6000 kilometres.

In the above formula, W is the mean kinetic energy of the granules which, according to the kinetic theory, is equal to the mean kinetic energy of a gas molecule at the same temperature. Therefore, $W = \frac{3}{2}\frac{RT}{N}$; since T, the temperature of the liquid, is known, and R is a constant, if we know W, we may find N from



Gamboge. Mastic.

Fig. 11.

$$N = \frac{3}{2} \cdot \frac{RT}{W}.$$

The evaluation of N is the test which Perrin always applies to his experimental observations. W is determined by observations of n_0/n, a, u, and h and then N is found from values of R, T, and W. The numbers above on being substituted in the formula give $N = 70{\cdot}5 \times 10^{22}$.

7. BROWNIAN MOVEMENT IN GASES.

It was pointed out first by Smoluchowski[23] that we should expect to have the Brownian movement in gases as well as in liquids, and he quotes from Bodaszewski[33] and O. Lehmann[34] references to the dancing movements executed by the particles of fumes of ammonium chloride, acids, phosphorus, etc., which they compared to the Brownian movement in liquids and interpreted as molecular movements. The formulæ of Smoluchowski and Einstein, given in section 5 (equations 7 and 10), are, in accordance with their proof, true whenever Stokes' law is applicable (vide Zeleny and McKeehan,[35] Perrin, Millikan,[36] and Lamb[37]). This law probably holds, approximately at least, for the smallest particles visible in the ultramicroscope; for liquids this will be true independently of the pressure, but for gases the truth of the statement depends on λ, i.e. on the pressure of the gas. Smoluchowski points out that, when the ratio of $\lambda : a$ becomes very large, the law of Stokes no longer holds, and the resistance to the motion of the particles must be determined by another method (Boltzman[38]); formula 4, section 5, then applies. In the motions in gases to which alone this formula applies, it may be used either for extremely small particles or for larger particles if the gas pressure is very much reduced.

Ehrenhaft[39] was the first to carry out direct measurements on the Brownian movement of particles in gases. He found that, as theory predicts, there is a much livelier motion in gases than in liquids; at the same time the action of gravity in causing vertical descent of the particles is also much more apparent in gases than it is in liquids. For comparatively large particles in the smoke of cigars and cigarettes and in the fumes of ammonium chloride, he observed an undoubted zig-zag Brownian movement, while with smaller particles obtained by a spark discharge between zinc, platinum, or silver electrodes, he found the motion very rapid. Ehrenhaft concludes that he has "proved without a doubt the existence of a motion in gases completely analogous to the Brownian movement in liquids".

As was predicted by Smoluchowski, it is more difficult to recognize this motion in gases on account of disturbing convection currents and the action of gravity. For the heavier particles, the velocity due to the force of gravity completely overshadows that due to the molecular shocks, while with the very small particles the opposite is the case. Table XII gives the velocities impressed by molecular shocks and by the force of gravitation, respectively, on silver particles of various sizes (density 10·5).

TABLE XII.—BROWNIAN MOVEMENT IN GASES.

Radius of the particles in cms.	Velocity in cms. per sec. due to molecular shocks $D_t = \sqrt{\frac{RT}{N} \cdot \frac{t}{3\pi\eta a}}$	Velocity in cms. per sec. due to gravity. $V = \frac{2}{9} \frac{a^2 . d . g}{\eta}$
1×10^{-7}	$6·3 \times 10^{-3}$	12×10^{-8}
5×10^{-7}	$2·8 \times 10^{-3}$	3×10^{-6}
1×10^{-6}	$2·0 \times 10^{-3}$	12×10^{-6}
5×10^{-6}	$8·9 \times 10^{-4}$	3×10^{-4}
1×10^{-5}	$6·3 \times 10^{-4}$	12×10^{-4}
5×10^{-6}	$2·8 \times 10^{-4}$	3×10^{-2}
1×10^{-4}	$2·0 \times 10^{-4}$	12×10^{-2}

For air, $\eta = 1·9 \times 10^{-4}$ (Poynting and Thomson [40]).

These numbers show that when we reach particles having diameters of the order of the wave-length of light the two velocities do not differ materially. As we deal with smaller particles, the velocity induced by gravity soon becomes negligible, while with particles increasing above 10^{-5} cms., the motion due to gravity soon dominates the situation. This is in keeping with what Ehrenhaft found: "Particles, the linear dimensions of which were of the order of the size of the mean free path of a gas molecule (1×10^{-5} cms.), and somewhat larger particles fall in a zig-zag line, the velocity due to gravitation being greater than that due to molecular shocks. Particles which near the limit of visibility in the ultramicroscope (1×10^{-7} cms.) are in such lively molecular motion that the vertical gravitational velocity is completely masked." Ehrenhaft viewed silver particles that remained in lively motion in the air of his ultramicroscopic cell for some thirty minutes. His measurements on the cigarette smoke particles gave a mean velocity of $2{\cdot}5 \times 10^{-3}$ cm./sec., and on the smaller particles of silver, $4{\cdot}6 \times 10^{-3}$ cm./sec.

Much interesting work has been done in this field by De Broglie.[41] Both Ehrenhaft and De Broglie have found that these silver particles, suspended in air, are charged and, by measuring the velocity impressed on them by a known electric field, have come to the conclusion that the charge is that of one electron. The values that they find for this charge, e, are respectively $4{\cdot}6 \times 10^{-10}$ and $4{\cdot}5 \times 10^{-10}$ electrostatic units (see also Millikan [38]).

8. COMPARISON OF THE VALUES OF N FOUND IN VARIOUS WAYS.

As we have seen, each of the formulæ deduced in relation to the Brownian movement involves the quantity N, the number of molecules in one gram-molecular weight of any substance. This number is associated with the theoretical explanation of a great variety of physical phenomena; some of these calculations are collected in Table XIII, along with certain other constants depending on N. The number of molecules in one c.c. of a gas at normal pressure and 0° C. (n), comes directly from the relation

$$N = 22400 \, . \, n.$$

N is also simply connected with the charge (e), on an electrolytic ion, e.g. of hydrogen. The decomposition by an electric current of one gram-molecule of hydrochloric acid requires a quantity of electricity equal to 96,550 coulombs—one faraday. Thus, one gram-atom of hydrogen (N atoms),

TABLE XIII.—VALUES OF THE MOLECULAR CONSTANTS, N, *n*, and *e*.

N.B.—The numbers in italics are those deduced directly from given experimental data. The other numbers are found from the two relations: $N \, . \, e = 29 \times 10^{13}$ and $N = n \, . \, 224 \times 10^{2}$.

Name.	Method.	$N \times 10^{-22}$	$n \times 10^{-19}$	$e \times 10^{10}$
Maxwell	Mean free path and density of liquid (Mercury).	*45*	2·0	6·5
Maxwell	Kinetic theory of gases.	*42·7*	1·9	6·8
Clausius-Mosotti	Dielectric constant of a gas.	*200*	9·0	1·4
Van der Waals	Value of "b"—oxygen and nitrogen.	*45*	2·0	6·5
	—Argon.	† *62*	† 2·7	† 4·67
Meyer	General results of kinetic theory.	*138*	6·1	2·1
Einstein-Perrin	Diffusion coefficient.	*40-90*	1·8-4·0	7·2-3·2
Rayleigh-Kelvin	Blue colour of the sky.	*54·9*	2·5	5·2
Rayleigh-Langevin	Blue colour of the sky.	*90*	4·0	3·2
Planck	Distribution of energy in the spectrum of hot bodies.	† *61·7*	† 2·8	† 4·69
Lorentz	Electron theory of radiation, long waves.	*77*	3·4	3·8
Lorentz-Fery	Same as above—Fery's nos.	† *66*	† 2·9	† 4·39
Pellat	Electrolytic ions.	*60-150*	2·7-6·6	4·8-1·9
Townsend	Cloud experiment.			
J. J. Thomson	" "	95·4	4·3	*3·0*
H. A. Wilson	" "	84·3	3·8	*3·4*
Millikan	" "	93·2	4·2	*3·1*
Begeman[42]	" "	† 62·3	† 2·8	† *4·65*
	" "	† 62·0	† 2·8	† *4·67*
Dewar-Rutherford	No. of rays in 1 c.c. of He.	† *57·3*	† 2·56	† 5·05
Boltwood-Rutherford	No. of atoms in the weight of Ra. disintegrated per yr. and the atomic wt. of Ra.	† *68·8*	† 3·1	† 4·21
Rutherford-Geiger	Direct determination of the charge on a particle.	† 62·3	† 2·8	† *4·65*
Regener[43]	Same as above.	† 60·5	† 2·7	† *4·79*
Moreau[44]	Charge on ions in flames.	† 67·3	† 3·0	† *4·3*
Perrin	Brownian movement of rotation.	*65*	2·9	4·5
Perrin-Dabrowski	Brownian movement in liquids.	† *71·5*	† 3·2	† 4·05
Perrin	Distribution of coll. particles.	† *70·5*	† 3·2	† 4·11
Chaudesaigues	Brownian movement in liquids.	† *64*	† 2·9	† 4·52
Ehrenhaft	Brownian movement in gases.	† 63·0	† 2·8	† *4·6*
De Broglie	Brownian movement in gases.	† 64·3	† 2·9	† *4·5*

in the state of ions carry one faraday and, therefore, in electrostatic units,

$$N \, . \, e = 96{,}550 \times 3 \times 10^{9} = 29 \times 10^{13}.$$

Consequently, having given one of the three quantities N, *n*, or *e*, we may easily determine the other two. In the results given in the table on next page these two relations have been used in deducing two of the three quantities from the third.

The numbers marked with a dagger are those which we have chosen as being, from an experimental point of view, of the greatest weight. Millikan,[36] in suggesting a similar set of results, discards Perrin's numbers for reasons which the latter[45] shows are due to misconceptions. The average values suggested by Rutherford,[46] Millikan, and from the above table are as follows:—

TABLE XIV.

Average.	$N \times 10^{-22}$	$n \times 10^{-19}$	$e \times 10^{10}$
Rutherford	62·3	2·77	4·65
Millikan	61·8	2·76	4·69
From Table	64·2	2·9	4·51

The general tendency of the results of recent electrical determinations of *e* has been to increase its value; $4{\cdot}6 \times 10^{-10}$ is probably not far from the true value of *e*. The corresponding value of N would be 63×10^{22}.

We have then all the data required to give the other important gas constants. The kinetic energy of agitation of a molecule equals $3/2 \,.\, RT/N$. The constant of molecular energy, $3/2 \,.\, R/N$, equals $1{\cdot}98 \times 10^{-16}$ erg. The mass of an atom of hydrogen equals $1\,.\,008/N = 1{\cdot}6 \times 10^{-24}$ gram.

The striking coincidence in the various best values of N, as shown in Table XIV, leaves little room for doubt that the Brownian movement, in both liquids and gases, is a direct result of molecular shocks on the suspended particles; conversely, the kinetic theory receives the most convincing, visible proof of its fundamental truths. The vast ramification of the kinetic theory in the domain of physics can hardly be illustrated better than in the work summarized in the results recorded in Table XIII (vide Larmor[4]).

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CHAPTER V.

THE OPTICAL PROPERTIES OF COLLOIDAL SOLUTIONS.

Apart from the interest developed by the ultramicroscope, the chief importance of colloidal solutions optically lies in their action on light which is incident upon them. The presence of the disperse phase in the medium changes the optical constants of the latter due to the absorption of the light; when the light absorbed lies in the visible region of the spectrum we have the colour of the solution by transmitted light determined chiefly by this absorption. This has led to much work on the colour of colloidal solutions.

At the same time the light which is reflected, or scattered diffusely from these solutions, is found to be, in general, partially polarized, and often completely plane polarized in a certain plane. This polarization of the scattered light is the second point of interest.

Some work has been done on the phenomenon of double refraction, both inherent in the solutions and artificially produced, and on the magneto-optical properties of the solutions containing the ferromagnetic elements.

I. Colour, Absorption, Scattering and Polarization of Light by Colloids.

The theoretical work on the optics of colloidal solutions deals almost entirely with the light which is scattered from a given sample; on the other hand, the experimental tests of the theory depend, with a few exceptions, on the determination of the curve of the absorption of the given sample. There is not necessarily a simple relation between these two quantities of light (see Steubing[1]). If we were dealing merely with the emergent transmitted light and the portion of the light which is prevented from passing through, we should have the relations shown in the accompanying table between the colour which is the result of the transmitted light (subjective) and the colour which would result from the combination of the light shut out (absorbed).

TABLE XV.—CORRESPONDING ABSORBED AND SUBJECTIVE COLOURS.[2]

Wave-length in μ.	·70	·65	·60	·55	·53	·50	·48	·45	·43	·40
Absorbed colour.	Purple	Red	Orange	Ye'low	Green yellow	Green	Green blue	Blue	Indigo	Violet
Subjective colour.	Green	Green blue	Blue	Indigo	Violet	Purple	Red	Orange	Yellow	Green yellow
Wave-length in μ.	·50	·48	·45	·43	·40	·70	·65	·60	·55	·53

However, this does not mean that the absorbed colour noted in the above table will give the colour of the scattered light; the latter is generally of a composite character due partly to ordinary absorption and reflection, and partly to selective reflection, and depends also on the refractive index of the supporting medium.

1. *Transmission, Absorption, and Reflection.*[3]—When a beam of light is allowed to pass through a layer of unit thickness of an absorbing substance a certain fraction a of the light is absorbed; a is known as the coefficient of transmission of the substance. If I_0 denotes the intensity of the initial beam and I the intensity of the beam after passing through a layer of thickness x cms., then $I = I_0\, a^x$. The quantity a varies with the wave-length of the light and the nature of the absorbing medium. If the incident beam consists of a mixture of light of various wave-lengths of intensities I_1, I_2, I_3, etc., for which the coefficients of transmission are a_1, a_2, a_3, etc., then

$$I = I_1 \, . \, a_1^x + I_2 \, . \, a_2^x + I_3 \, . \, a_3^x \; + \text{etc.}$$

The quantity and quality of the transmitted light varies with the composition of the incident beam, i.e. with the nature of the source, with the nature of the absorbing medium, and with the thickness traversed.

On account of the fact that a depends on the wave-length, light of different colours will be absorbed to different extents and, consequently, the emergent light will be coloured; this colour will be, in general, the same for all thicknesses traversed, the tint deepening as the thickness of the absorbing layer is increased. A curious result ensues if the values of I and a for the various component wave-lengths are such that the corresponding values of $I \cdot a^t$ change relatively to one another as the thickness increases; as a consequence, the colour of the emergent light may change completely as the thickness of the absorbing layer is increased. For example, cobalt glass, while transmitting both blue and red light, absorbs the blue more than the red; when the thickness is large the blue rays are almost entirely cut out and the glass appears red by transmitted light; when the thickness is small, the glass is blue by transmitted light (see also Wood [4]).

The sum total of the light cut off by an absorbing layer is composite in its nature—a part is extinguished in the medium itself, and a part is reflected from the surface or from the interior of the medium; this reflected portion may consist of light in which all wave-lengths are reflected in the same proportion, or we may have, as in the case of some aniline dyes, gold, copper, etc., selective reflection, i.e. light of certain wave-lengths being reflected more strongly than that of other wave-lengths.

Ordinarily bodies are made visible by the light which is diffusely reflected from their surfaces and from structural inequalities in the interior. The part that is reflected from the interior suffers absorption by the medium after such reflection and consequently the reflected light is in general coloured. If the medium consists of particles or films which have little depth of the substance, as in clouds or in the froth on a liquid, the absorption of the internally reflected light is negligible and the colour of the reflected light is white if the incident light is white.

"Reflection then is the proximate cause of colour in these bodies, inasmuch as without reflection no light would reach the eye, but absorption is the ultimate cause, for it is thus that the reflected light is deprived of some of its constituents and becomes coloured" (Preston [3]).

Following out a similar line of reasoning, Wood says: "Absorption is not the only factor which determines this selective reflection, and we often find misleading statements in text-books on optics, it being frequently stated that the wave-lengths most copiously reflected are the ones most strongly absorbed. This is by no means the case. . . . In the case of absorbing media, the reflecting power depends both on the refractive index and the coefficient of absorption. Now, absorbing media have a high refractive index on the red side of the absorption band and a low index on the blue side; consequently the spectrum of the reflected light will be brightest on the red side of the absorption band, since for these wave-lengths we have a large coefficient of absorption and a high refractive index. On the blue side, however, the low value of the index diminishes the reflecting power more than the augmentation due to the powerful absorption. The hue of surface colour thus depends on the refractive index of the medium in which the substance is immersed, for it is the relative and not the absolute refractive index with which we are concerned."

2. *The Blue Colour of the Sky—Artificial Atmospheres.*—The interest in the colours produced by turbid media was, in the first place, due to the repeated attempts to explain the blue colour of the sky. Various explanations of the latter phenomenon have been put forward; that which is generally accepted at the present time was first suggested by Leonardo da Vinci [5]: namely, that the atmosphere is in reality a turbid medium, filled with particles of dust, globules of water, etc., and, in accord with the action of such media on light passing through them, diffuses laterally light which is richest in the blue tints, while the light which is directly transmitted tends to have the red most intense. This explanation has been experimentally confirmed by the action of artificial atmospheres of turbid liquids and vapours prepared by Brücke,[6] Roscoe, and Tyndall,[7]

and strengthened, on the theoretical side, by the mathematical treatment of Rayleigh[8]; indeed, Rayleigh's most recent contribution[9] to the subject is that the colour of the atmosphere may possibly be explained by the scattering action of the air molecules themselves.

In one of his experiments on artificial atmospheres, Tyndall passed light through a tube into which he had introduced a mixture of air bubbled through nitrate of butyl and air (in excess) bubbled through hydrochloric acid, the total pressure in the tube being about 1 cm. of mercury. On allowing the light from an arc lamp to traverse the tube, chemical action of the two vapours ensued, and a very fine cloud of solid particles began to form. At first the particles were exceedingly small and the colour observed laterally was a delicate blue, but as the experiment progressed, the particles gradually increased in size, the colour gradually brightened, "still maintaining its blueness, until at length a whitish tinge mingled with the pure azure, announcing that the particles were now no longer of that infinitesimal size which scatters only the shortest waves". Similar artificial atmospheres may be made in water by the addition of a few drops of alcoholic solution of mastic, or by the production of fine sulphur particles due to the interaction of dilute solutions of sodium hyposulphite and hydrochloric acid.

The light scattered by the incipient cloud is partially plane-polarized—the maximum percentage of polarization being produced at points in the plane at right angles to the direction of the incident light; the plane of polarization in the scattered light is that containing the beam of light and the eye of the observer. As the particles in suspension grow in size, the polarization becomes less complete while the lines along which it is a maximum shift away from the position of 90° to the direction of the incident beam. Tyndall found also that there always existed neutral points where the polarization was zero and such that in passing through the neutral point the planes of polarization turned through a right angle; this is in keeping with the observations of Arago,[10] Babinet,[11] and Brewster[12] on neutral points in the light from the sun.

3. *Solutions and the Tyndall Phenomenon.*—The fact that the so-called Tyndall phenomenon is shown by particles very much below the microscopic, or even ultramicroscopic, limit was used by Linder and Picton [13] in their experiments on arsenious sulphide solutions. By preparing such solutions with different grades of dispersion, they offered strong evidence of the continuity of the transition from coarse suspensions to crystalloidal solutions; they classified their various arsenious sulphide solutions thus:

As_2S_3 (α)—aggregates visible under the ordinary microscope,

As_2S_3 (β)—aggregates invisible but not diffusible,

As_2S_3 (γ)—aggregates diffusible but held by filter,

As_2S_3 (δ)—aggregates diffusible and not held by filter but showing the Tyndall phenomenon.

More recently still Spring,[14] Lobry de Bruyn [15] and their co-workers have examined all types of solutions for the Tyndall effect. Tyndall himself remarked that almost all liquids have motes in them sufficiently numerous to polarize the light sensibly; and very beautiful effects may be obtained by simple artificial devices. When, for example, a cell of distilled water is placed in front of the electric lamp, and a narrow beam permitted to pass through it, scarcely any polarized light is discharged, and scarcely any colour produced with a plate of selenite. But while the light is passing through it, if a piece of soap be agitated in the water above the beam, the moment the infinitesimal particles reach the beam the liquid sends forth laterally almost perfectly polarized light; and if the selenite be employed, vivid colours flash into existence. A still more brilliant result is obtained with mastic dissolved in a great excess of alcohol.

"The selenite rings constitute an extremely delicate test as to the quantity of motes in a liquid. Commencing with distilled water, for example, a thickish beam of light is necessary to make the polarization of its motes sensible. A much thinner beam suffices for common water; while with Brücke's precipitated mastic, a beam too thin to produce any sensible effect, with most other liquids, suffices to bring out vividly the selenite colours."[7]

By this effect Spring showed the presence of the aggregates of hydrates resulting from the hydrolysis of dissolved salts, and suggested the Tyndall effect to explain gold ruby glass and other metal glasses; he defined a true solution to be one which does not show the Tyndall effect. Lobry de Bruyn and Wolff found that aqueous solutions of saccharose, raffinose, etc., in high concentration, gave this diffusely scattered light. Doubtless the recognition of the scattered light has depended on the intensity of the illumination from the source and on the sensitiveness of the apparatus used by the various workers for detecting the same. It has been shown recently that, as already noted by Tyndall, it is exceedingly difficult to get even distilled water which does not show some faint indication of the Tyndall phenomenon.

4. *Theoretical Work on the Scattering of Light by small Particles.*—The theoretical importance of the optics of colloidal solutions was first noted by Faraday,[16] and became a subject of his research about 1856. He gives the reasons which led him to this inquiry in the following language:—

"Light has a relation to the matter which it meets with in its course, and is affected by it, being reflected, deflected, transmitted, refracted, absorbed, etc., by particles very minute in their dimensions. The theory supposes the light to consist of undulations, which, though they are in one sense continually progressive, are, at the same time, as regards the particles of the æther, moving to and fro transversely. The number of progressive alterations or waves in an inch is considered as known, being from 37,600 to 59,880, and the number which passes to the eye in a second of time is known also, being from 458 to 727 billions; but the extent of the lateral excursion of the particles of the æther, either separately or conjointly, is not known, though both it and the velocity are very small compared to the extent of the wave and the velocity of its propagation. Colour is identified with the number of waves. Whether reflection, refraction, etc., have any relation to the extent of the lateral vibration, or whether they are dependent in part upon some physical action of the medium unknown to or unsuspected by us, are points which I understand to be as yet undetermined.

"Conceiving it very possible that some experimental evidence of value might result from the introduction into a ray of separate particles having great power of action on light, the particles being at the same time very small compared to the wave-lengths, I sought among the metals for such. Gold seemed especially fitted for experiments of this nature because of its comparative opacity amongst bodies, and yet possession of a real transparency; because of its development of colour in both the reflected and transmitted ray; because of the state of tenuity and division which it permitted with the preservation of its integrity as a metallic body; because of its supposed simplicity of character; and because known phenomena appeared to indicate that a mere variation in the size of its particles gave rise to a variety of resultant colours. Besides, the waves of light are so large compared with the dimensions of the particles of gold which in various conditions can be subjected to a ray, that it seemed probable that the particles might come into effective relations to the much smaller vibrations of the æther particles; in which case, if reflection, refraction, absorption, etc., depended upon such relations, there was reason to expect that these functions would change sensibly by the substitution of different sized particles of this metal for each other."

Similar language might very well indicate the purpose of workers who have attempted, since Faraday's time, to explain optical properties of the metal sols from the electromagnetic point of view.

Optically, the important points of Faraday's experiments on gold colloidal solutions are his proofs that such solutions containing the smallest particles of gold have red or ruby tints by transmitted light, while if, for any reason, the particles become larger and larger, the colour by transmitted light tends more and more to the blue.

The first attempt to give a mathematical explanation of the action of turbid media on light is that of Rayleigh[1, 2], first in the language of the undulatory theory simply and later from the point of view of the electromagnetic theory. He assumes that the foreign obstructing matter, supposed to be present in the form of electrically non-conducting particles, each small in comparison with the wave-length of the light used, loads "the ether so as to increase its inertia without altering its resistance to distortion. If the particles were away the waves would pass on unbroken, and no light would be emitted laterally. Even with the particles retarding the motion of the ether the same will be true if, to counterbalance the increased inertia, suitable forces are caused to act on the ether at all points where the inertia is altered. These forces have the same period and direction as the undisturbed luminous vibrations themselves. The light actually emitted laterally is thus the same as would be caused by forces exactly the opposite of those acting on the medium otherwise free from disturbance, and it only remains to see what the effect of such forces would be. In the first place there is necessarily a complete symmetry around the direction of the force; the disturbance, consisting of transverse vibrations, is propagated outwards in all directions from the centre; and in consequence of the symmetry the direction of the vibration in any ray lies in the plane containing the ray and the axis of symmetry; that is to say, the direction of vibration in the scattered or refracted ray makes with the direction in the incident or primary ray the least possible angle. The symmetry also requires that the intensity of the scattered light should vanish for the ray which would be propagated along the axis. For there is nothing to distinguish one direction transverse to the ray from another. Suppose for distinctness of statement that the primary ray is vertical, and that the plane of vibration is that of the meridian. The intensity of the light scattered by a small particle is constant, and a maximum for rays lying in the vertical plane running east and west, while there is no scattered ray along the north and south line. If the primary ray is unpolarized, the light scattered north and south is entirely due to that component which vibrates east and west, and is therefore perfectly polarized, the direction of its vibration being east and west. Similarly any other ray scattered horizontally is perfectly polarized, and the vibration is performed in the horizontal plane. In other directions the polarization becomes less and less complete as we approach the vertical."

As a result of the analysis, Rayleigh shows that the intensity I_s of the scattered light varies according to the following law:—

$$I_s \propto I \,.\, \frac{(D' - D)^2}{D^2}(1 + \cos^2\beta)\frac{m \,.\, \pi \,.\, T^2}{\lambda^4}\,;$$

where I = intensity of the incident light,

D' and D = the optical density of the particles and the dispersion media respectively (proportional to the squares of the corresponding indices of refraction),

m = number of particles per unit volume,

T = volume of a disturbing particle,

λ = the wave-length of the scattered light,

β = the angle between the line of sight and the incident direction.

It is at once apparent that from ordinary white light incident on such a medium, the percentage of red light (·75 μ) reflected would be about one-twelfth that of the violet (·40 μ); for a given mass of the disperse phase per unit volume, m T = a constant, and therefore I^s varies directly as T; for the number of particles per unit volume constant, i.e. m = a constant, I_s varies directly as T^2. These conditions are quite in agreement with the phenomena described by Tyndall in his experiments.

When scattering alone is considered, the intensity of the scattered light, I_s, varies inversely as the fourth power of the wave-length.[17] "Now the light which reaches the eye is scattered, and also transmitted (both before and after scattering) through some thickness x of the medium. Hence its composition will be determined by finding the effect of transmission on the quantity I_s. This problem is equivalent to that of finding the intensity of a pencil of light after transmission through an absorbing medium when the absorption varies inversely as the fourth power of the wave-length. Hence we have

$$\frac{dI}{I} = -\frac{k \, . \, dx}{\lambda^4},$$

where k is a constant, and dI the change of intensity in passing through a layer of thickness dx. The intensity of the light reaching the eye, after suffering scattering as well as transmission through a total thickness x of the medium, is therefore

$$I = I_s \, . \, e^{-\frac{kx}{\lambda^4}},$$

and expressing I_s in terms of $\frac{1}{\lambda^4}$, we have finally

$$I = \frac{A}{\lambda^4} \, . \, e^{-\frac{kx}{\lambda^4}}.$$

This expression exhibits the joint effects of scattering and transmission, and shows how I diminishes for large values of the wave-length as well as for small values. The maximum value of I corresponds to some intermediate wave-length λ_m given by the equation

$$\lambda_m{}^4 = k \, . \, x,$$

which gives the maximum value of I,

$$I_m = A \, . \, \lambda_m^{-4} \, . \, e^{-1} = \frac{A}{e \, . \, k \, . \, x}$$

while the intensity I corresponding to any wave-length λ is related to I_m by the equation

$$\frac{I}{I_m} = \frac{\lambda_m^4}{\lambda^4} \, . \, e^{1 - \frac{\lambda_m^4}{\lambda^4}} \, . \text{[17, 18]}$$

The curve in Fig. 12 shows the relation between I and I_m given by the last formula for the case of the maximum scattering taken arbitrarily at the wave-length of 5×10^{-5} cm. The resulting curve is quite typical of the experimental curves obtained in the determination of the absorption of metal glasses and colloidal solutions.

The Rayleigh formula has been tested as to the plane polarization being complete along a line at right angles to the incident light and quite well confirmed; by Ehrenhaft,[19] who obtained for silicic acid 90°, and for arsenic sulphide 87°, by Bock [20] on particles in a steam jet and as to the polarization in various directions, i.e. β varying, by Dimmer[21] on glasses of different sorts.

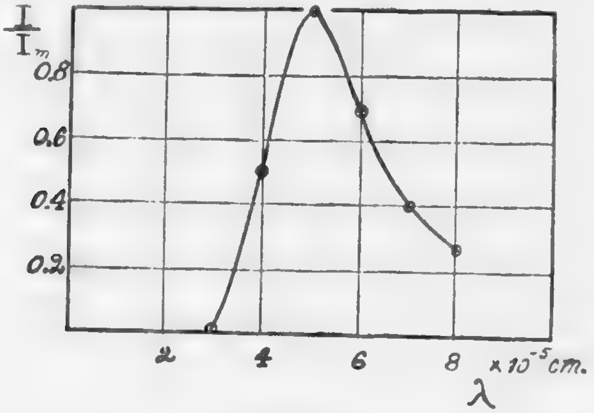

FIG. 12.

The investigation of Professor J. J. Thomson[22] on the analogous effect of conducting particles scattered throughout a given medium, treated electromagnetically, leads to a variation in the position of the lines of maximum polarization.

"The scattered light produced by the incidence of a plane polarized wave vanishes in the plane through the centre at right angles to the magnetic induction in the incident wave along a line making an angle of 120° with the radius to the point at which the wave first strikes the sphere and it does not vanish in any direction other than this. Thus, if non-polarized waves of light or of electric displacement are incident upon a sphere whose radius is small compared with the wave-length of the incident vibration, the direction in which the scattered light is plane polarized will be inclined at an angle of 120° to the direction of the incident light. The scattering of light by small metallic spheres thus follows laws which are quite different from those which hold when the scattered light is produced by non-conducting particles. In the latter case (Rayleigh, Phil. Mag., V. 12, p. 81, 1881) when a ray of plane polarized light falls on a small sphere, the scattered light vanishes at all points in the plane normal to the magnetic induction when the radius vector makes an angle of 90°, and not 120°, with the direction of the incident light. Thus when non-polarized light falls on a small non-conducting sphere, the scattered light will be completely polarized at any point in a plane through the centre of the sphere at right angles to the direction of the incident light.

"When the light is scattered by a conducting sphere, the points at which the light is completely polarized are on the surface of a cone whose axis is the direction of propagation of the incident light and whose semi-vertical angle is 120°."

This result was tested experimentally by Threlfall and Professor Thomson [23] with negative results, but on the other hand, it has been partially confirmed by the recent experimental results of Ehrenhaft [19] and Müller.[24] In the light of the following comment by Professor Thomson on the above theory, it is easily possible that such a variation in experiments may still be quite consonant with the theory.

"I made, about two years ago, some rough experiments on the polarization of light scattered by small particles of gold, the results of which were in agreement with those of Professor Threlfall. I regarded these experiments as confirming the results of Maxwell and Wien, that the resistance of metals to very rapidly alternating currents which constitute light is much greater than to steady currents.

"It is moreover very difficult to make these experiments so as to be a fair test of the theory, as it is only when the size of the particles is within narrow limits that the theory would be applicable, even supposing the resistance to be as low as for steady currents. To scatter the light the diameters of the particles must be small compared with the wave-length of light, while the theory given in my 'Recent Researches on Electricity and Magnetism' requires that the depth to which the currents produced by the light penetrate the particle should be small fraction of the radius of the particle. Now at a depth d below the surface of the sphere the intensity of the induced current varies as e^{-kd}, where $k = [2\pi\mu\rho\,\sigma]^{\frac{1}{2}}$, μ being the magnetic permeability, σ the specific resistance of the metal, and $2\pi\,\rho$ the time of oscillation of the incident electrical vibration. Thus the currents at a depth $1/k$ below the surface will be only $1/e$ of their value at the surface; we may therefore take $1/k$ as the measure of the thickness of the film filled by the currents. For gold $\sigma = 2100$ for steady currents, $\mu = 1$, and for the D line $\rho = 2\pi \times 5{\cdot}097 \times 10^{14}$; thus $1/k = 3{\cdot}2 \times 10^{-7}$. The wave-length of the D line is $5{\cdot}89 \times 10^{-5}$, about 170 times $1/k$. Thus for the theory to be applicable, the diameter of the particles must be small compared with λ and large compared with $1/k$. As $1/\lambda$ is only 170 times $1/k$ this makes the range of diameters very small. A more satisfactory test of the theory could be made with longer wave-lengths and larger particles; for the thickness to which the currents descend varies as the square root of the wave-length, so that the ratio of the wave-length to the thickness of the current film increases as the wave-length increases."

As pointed out here, and also in the discussion between Ehrenhaft and Pockels,[25] regarding the former's experimental confirmation of the theory, there is the indeterminate quantity, σ, the specific conductivity of the metal spheres for the electric waves in the light waves which renders agreement with the theory rather fortuitous; there is a very limited range of sizes of particles for which the maximum polarization will, even theoretically, be in a direction making 120° with the incident direction.

The invention of the ultramicroscope with the consequent power afforded for measuring with considerable accuracy the size of the particles in colloidal solutions, both solid (metal glasses) and liquid, stimulated the interest in the optical properties of these suspensions. The metal glasses and metal sols offer the greatest variety of colour effects; many of the sols, the disperse phases of which are compounds, and practically all emulsoids, are either colourless or merely milky white; the latter probably contain particles which are too large to scatter the blue light sufficiently in excess to make the colour distinctive, or the indices of the disperse phase and the medium may be so nearly equal that the term $(D' - D)/D$, in the Rayleigh formula, is nearly zero.

The problem of the colour of the metal sols and glasses is rendered complex on account of the many varying influences to be taken into consideration. In the first place, the relation of the size of the particle to the wave-length of the light used is all-important; to apply Rayleigh's or Thomson's theory of scattering, the particles must be small in comparison with the wave-length. For a given number of particles per unit volume, the intensity of the scattered light varies directly as the sixth power of the diameter and inversely as the fourth power of the wave-length; that is, it is the light of short wave-length that is most abundantly scattered, and the intensity of the scattered light, and therefore also of the absorption, increases rapidly with the diameter of the small particles. However, as the particles approach the dimensions of the wave-length, we shall have ordinary reflection phenomena (including selective reflection) coming into play; in which case, the intensity of the diffused light (and therefore also the amount of the absorption varies, in general, according to the law

$$R = 100 - \frac{\text{Constant}}{\sqrt{\lambda}},$$

for a given metal; i.e. the greater the wave-length, the greater the scattered or reflected light; in addition, the reflected light now varies as the square of the diameter. The transition from samples with extremely small particles to those with particles of microscopic size affords an infinite variety of possibilities in their absorption.

Again, as a consequence of Rayleigh's formula (p. 101), there is some wave-length, not necessarily in the visible region of the spectrum, for which, with scattering alone, we should get a maximum intensity.

In the third place, we must always take into consideration, not only the relation between the refractive indices of the metal particles and the supporting medium for a single value of the wave-length, but also the dispersions of the two substances. As pointed out by Christiansen,[26] if powdered glass particles (of dimensions comparable with the wave-length of light be suspended in a liquid of identically the same refractive index for some standard wave-length, colour will still be produced, on account of the difference in the dispersions of the liquid and the glass. Similarly, with a suspension of copper particles in water, if there were no other modifying cause, only the wave-length for which the index of refraction of copper is equal to that of water would be transmitted unchanged (*vide* Garnett [27]).

Finally, in the discussion from an electromagnetic point of view, it is apparent that variations in such features as the surface, shape, etc., of the particles will make large changes in the optical constants of the solution, and consequent variations in the absorption of light.

This complexity has necessitated the attack being made initially with very simple assumptions. The first of the more recent attempts to solve the problem of the variations in the colour of these suspensions is that of Garnett.[27] He dealt more particularly with metal glasses (gold, silver, and copper) and the metal sols of gold and silver. The object of his work was "to obtain information concerning the ultramicroscopic structure of various metal glasses, colloidal solutions, and metallic films, by calculating optical properties corresponding to certain assumed microstructures, and by comparing the calculated properties with those observed". Calculations were made for three types of microstructure, (1) that in which the metal molecules were distributed at random (called by Garnett, amorphous), (2) that in which the metal molecules were arranged in small spherical groups, many to a wave-length of light (granular), and (3) that in which the small spheres were replaced by small spheroids (spicular).

Following Lorenz, Hertz, and Rayleigh, Garnett first shows that a metal sphere, small compared with the wave-length of light, produces in all surrounding space the same effect as would be produced by a Hertzian doublet placed at its centre. If light of wave-length λ falls upon a sphere of metal of radius a, of refractive index n, and of extinction coefficient k, then the complex dielectric constant ϵ will be expressed by

$$N = n(1 - ik) = \sqrt{\epsilon}\,; \ (i = \sqrt{-1}).$$

If there be M such spheres per unit volume, *in vacuo*, Garnett shows that considering a volume which in all its directions is great compared with the wave-length of light, this complex medium is optically equivalent to a medium of refractive index n' and extinction coefficient k' given by the equation

$$N' = n'(1 - ik') = \sqrt{\epsilon'}$$

where

$$\epsilon' = 1 + \frac{4\pi M a^3 \cdot \frac{N^2 - 1}{N^2 + 2}}{1 - \frac{4\pi}{3} M a^3 \frac{N^2 - 1}{N^2 + 2}};$$

or, if μ = the volume of metal per c.c. of the solution, $[\mu = \frac{4}{3}\pi a^3 M]$

$$\epsilon' = 1 + \frac{3\mu \frac{N^2 - 1}{N^2 + 2}}{1 - \mu \frac{N^2 - 1}{N^2 + 2}}.$$

If the metal spheres be situated in glass of refractive index ν instead of *in vacuo*, the equation becomes

$$[n'(1 - ik')]^2 = \epsilon' = \nu^2 + \frac{3\mu\nu^2 \cdot \frac{N^2 - \nu^2}{N^2 + 2\nu^2}}{1 - \mu \cdot \frac{N^2 - \nu^2}{N^2 + 2\nu^2}}.$$

"The constants, n' and k' of the medium thus depend only on μ, the relative volume of metal, and not on the radii of the individual spheres. It is clear that the spheres may now be supposed to be of quite various radii, provided only that there be many to the wave-length of light in the medium."

In the cases under consideration, metal glasses and metal sols, the fraction μ is always small; neglecting in the latter equation, $\mu \cdot \frac{N^2 - \nu^2}{N^2 + 2\nu^2}$ in comparison with unity, we may write

$$[n'(1 - ik')]^2 - \nu^2 = 3\mu\nu^2 \cdot \frac{N^2 - \nu^2}{N^2 + 2\nu^2} = \text{say, } 3\mu\nu^2(a - 2i\beta).$$

Equating real and imaginary parts, we get expressions for a and β in terms of n, k, and ν. Introducing at each step the fact that μ is a small quantity, the analysis gives

$$n'k' = 3\mu\nu\beta \text{ and } n' = \nu(1 + \tfrac{3}{2}\mu a).$$

That is, knowing the values of n and k for the metal (as found from other independent experiments), we may determine the values of $n'k'$ and n' for the complex medium. The above applies to the metal in what Garnett calls the granular state.

For the amorphous state of subdivision of the metal, i.e.

suspended as a molecular solution, taking for the constants of the solution n'', k'', N'', ϵ'', we have

$$N'' = n''(1 - ik'') = \sqrt{\epsilon''},$$

and the corresponding equations:—

$$[n''(1 - ik'')]^2 - \nu^2 = (2 + \nu^2)\mu \,.\, \frac{N^2 - \nu^2}{N^2 + 2\nu^2} = \text{say}, (2 + \nu^2)\mu \,.\, (\alpha' - 2i\beta').$$

Again, equating real and imaginary parts, we may obtain α' and β' in terms of n, k, and ν, and the resulting equations,

$$n''k'' = \frac{2 + \nu^2}{\nu} \,.\, \mu\beta' \text{ and } n'' = \nu\left(1 + \frac{2 + \nu^2}{2\nu^2} \,.\, \mu\alpha'\right).$$

Garnett shows that the expressions $n'k'$ and $n''k''$, measure the absorption in the granular and amorphous states respectively; that is, "when light of a wave-length λ traverses a thickness d of a metalliferous medium, the intensity of the light is reduced in the proportion

$$e^{-4\pi d}\ \frac{n''k''}{\lambda} \text{ or } e^{-4\pi d}\,\frac{n'k'}{\lambda},$$

according as the metal is in true solution or in spherical aggregates".

The above theory lends itself to experimental confirmation by the calculation of the absorption produced by a given solution containing what are known to be fine particles, and comparing these calculations with the results of experiment. A very exhaustive series of such experiments was carried out by Garnett on gold, silver, and copper glasses, and gold and silver colloidal solutions. In general there is a striking agreement between the calculated and the observed results.

It will be noticed from Garnett's formulæ that the refractive index of the complex medium which has the metal in molecular solution is different from that in which the metal is in the form of small spheres. Garnett's experiments on the refractive indices of colloidal silver solutions for the sodium yellow line gave values exceedingly near the value n', calculated from the distribution of spheres; he consequently concludes "that practically the whole of the silver must have been in suspension in the form of small spheres".

As the whole of Garnett's treatment relates to the phenomena observed with spheres small compared with the wave-length of light in the medium. Spence[28] extended it experimentally by using infra-red rays, of wave-length up to 18×10^{-5} cm. and determining the absorption of Bredig metal sols of gold, platinum, and silver. However there was the additional difficulty that the liquid media themselves absorbed these rays to a certain extent. Spence extended Garnett's theoretical work to include the case of the supporting media itself showing absorption of the rays used. If the complex dielectric constant of the medium be written

$$\epsilon''' = \nu(1 - ig),$$

we shall have the dielectric constant of this medium when the spheres are distributed in it given by the equation

$$\epsilon' = \epsilon''' + \frac{3\epsilon'''\mu \cdot \left[\dfrac{\epsilon - \epsilon'''}{\epsilon + 2\epsilon'''}\right]}{1 + \mu \cdot \left[\dfrac{\epsilon - \epsilon'''}{\epsilon + 2\epsilon'''}\right]}.$$

Following out Garnett's analysis and keeping in mind the negligible quantities involved in relation to colloidal solutions, Spence gets for the refractive index, n, of the metal in the solution, the equation

$$n = \frac{9\nu^3\mu}{2a(t - w)} + \sqrt{\left[\frac{9\nu^3\mu}{2a(t - w)}\right]^2 - \frac{(a^2 - 2\nu^2)^2}{a^2}}$$

—the root of a quadratic equation in n.

where $a = kn$ = the absorption coefficient of the metal,

ν = the refractive index of the medium itself,

$t = k'n'$ = the absorption coefficient of the colloidal solution,

$w = g\nu$ = the absorption coefficient of the supporting medium.

When n is considerably less than 1, the quadratic equation reduces to

$$n = \frac{(t - w)(a^2 - 2\nu^2)^2}{9a\nu^3\mu}.$$

Two results are immediately deducible from the theory: (1) the value of $(t - w)$, the difference between the absorptions of the colloidal solution and the supporting medium is directly proportional to μ, the concentration; (2) the value of n obtained for a given metal should be independent of the supporting medium. Spence confirmed both of these points experimentally for wave-lengths up to 18×10^{-5} cm. He obtained the indices of refraction for gold, silver, and platinum in solutions with water and ethyl malonate, respectively, as the supporting media; his values agreed well among themselves and also with corresponding values found by other workers by more direct methods. As an additional test of his results, he calculated the value of R in Drude's equation

$$R = \frac{(n^2 - 1)^2 + a^2}{(n^2 + 1)^2 + a^2},$$

where R is the reflection coefficient and a the absorption coefficient and found close agreement between his results and those observed by others.

By calculating the light scattered by small particles of a colloidal solution as a series of partial wavelets of two groups, viz., those corresponding respectively to the electric and magnetic vibrations of the particles, Mie[29] has determined the optical properties of turbid media, in which the particles may be regarded as spherical and for which the turbidity is infinitely thin optically, such as is the case with ordinary colloidal solutions. Only a finite number of these partial waves need be taken into account in these cases; in any case, the $(r - 1)$th magnetic vibration is considered simultaneously with the rth electric vibration. For colloidal solutions with very fine particles only the first electric vibration need be considered; this corresponds to the Rayleigh scattering. With coarser particles one must also take account of the first magnetic and the second electric vibrations. If an unpolarized beam of light is passed through a colloidal solution, the laterally scattered light is completely or partially plane polarized, but never elliptically polarized; this seems to be borne out by the consensus of experimental results. For gold solutions with particles (spherical) up to about 100 $\mu\mu$ in diameter, the light scattered laterally gives only the Rayleigh beams, the maximum polarization (almost 100 per cent) occurring at 90°. As the particles increase in size, the amount of unpolarized light in the plane at 90° to the incident direction increases very rapidly and the lines of maximum polarization move towards a larger angle than 90°, until for particles of 160 to 180 $\mu\mu$ diameter, they lie between 110° and 120° to the incident direction. As shown also by the Rayleigh formula, for constant concentration the scattered radiation of very fine turbidities is proportional to the volume of the very fine particles. In coarser sols, the scattered light grows slowly with increasing size of particle and finally reaches a maximum, which depends on the wave-length ; with gold particles, the maximum scattering is given by particles with diameters between 1/4 and 1/3 of the wave-length in the dispersion medium. Mie finds that results do not justify the assumption that the particles are perfectly conducting spheres. The scattered light from gold particles is generally much stronger than would be expected from perfectly conducting spheres of the same size. In addition, with the finest subdivision of the gold, the scattered light shows a very distinct maximum in the greenish yellow rather than in the blue violet. The absorption of colloidal gold solutions depends on two properties of metallic gold, the ability to absorb light and to reflect light. Solutions, in which the diffuse reflection is small compared with the proper absorption, show the absorption maximum of the gold particles, which lies in the green ; by transmitted light they are ruby red. Solutions which show strong diffuse reflection appear by transmitted light blue, because gold reflects chiefly the reddish yellow light.

Steubing, a pupil of Mie,[1] was the first to measure quantitatively the intensity of the scattered light, as well as that of the transmitted light. Working with various gold sols, he found that as a general thing, only a small portion of light was lost by scattering, the greater part of the light cut out being destructively absorbed in the metal. This result bears out the views expressed by Mie[2] and Pockels[3] that the explanation of the colours by resonance is not possible. In addition to finding the absorption maxima for different sols, Steubing measured the polarization of the scattered light ; he found it to be partially plane polarized, the direction of the maximum polarization being at 90° to the incident beam and amounting to about 90 per cent of the total light in that direction. Contrary to the results of others he found that certain gold sols, blue by transmitted light, contained extremely fine particles.

Gans and Happel[30] extended Garnett's and Mie's theoretical work so as to make the theory applicable to concentrated solutions and also to sols containing particles not small compared with the wave-length of the light. They deduced formulæ for the refractive index of a colloidal solution and the absorption per unit length (not to be confused with the absorption coefficient). They applied their formula to two special cases, (1) an infinitely dilute solution containing particles of various sizes, and (2) solutions containing infinitely small particles but of varying concentrations. Later Gans[31] extended Mie's work to apply to ellipsoidal particles, and found that the absorption curves moved forward to the larger wave-lengths as the particles departed from the spherical form. He concludes that the fine particles in Steubing's blue solutions were probably ellipsoidal. In a still later paper,[32] the same author gives the curves of absorption of silver sols consisting of ellipsoidal particles, from numbers calculated by Müller.[24] Supposing that the particles are ellipsoids of revolution with the ratio of the axes A : B, a variation in the value of A : B gives surprising variety in the form of the theoretical absorption curve.

Lampa[33] attacked the same problem of determining the absorption and refraction coefficients of an ideal colloidal solution from an independent point of view. He began with Hasenorhl's calculations of the changes suffered by a plane polarized electromagnetic wave traversing a medium—an ideal gas—composed of uniformly distributed spheres with dielectric constant, permeability, and conductivity different from those of the supporting medium. His expressions for the optical constants of a dilute colloidal solution are shown to be identical with the analogous expressions given by Mie, and Gans and Happel. Experimenting on a red colloidal gold solution containing ·011 grm. of gold per 100 c.cs., he found that the observed absorption curves were similar to the calculated curves but not coincident with them (see also Rolla[34]).

Lampa[35] and Robitschek[36] have shown by ingenious experiments that the red gold solutions (transmitted light) consist of finer particles than the blue solutions. By centrifuging a sample of blue solution, Lampa showed that the transparency towards the red increases as the centrifuging proceeds, and that, therefore, since the larger particles are expelled from the solution first, the red solution contains the smaller particles. Robitschek found in the centrifuge tube a gradation from red transparency at the top of the tube to blue transparency at the bottom after a sample had been centrifuged for some time.

We may safely conclude that, in general, there is a direct connexion between the size of the particles in metallic colloidal solutions as worked out particularly for gold solutions; but that any rule defining this connexion is bound to have exceptions introduced when the particles depart from the spherical form.

In his work on the proof of the continuity of physical properties and molecular solutions, Svedberg[37] has performed two series of experiments on the optical properties of colloidal solutions; (1) colorimetric, and (2) spectrophotometric. In the first series he determines the limit of the visibility of the colour produced by various solutions of gold containing particles of different sizes. It is often found in comparing the colour-intensity of colloidal and molecular solutions of the same substance that the colloidal solution is much more strongly coloured than the corresponding molecular solution of the same concentration ?). Svedberg shows that, with decreasing size of particles (i.e. increasing dispersion grade), from a certain size down to the molecular size the colour-intensity continually decreases; in some cases he found that, with decreasing size of particles, the colour-intensity finally approaches very rapidly that of the corresponding molecular system.

In his rather less satisfactory spectrophotometrical observations he measured the absorption of the principal mercury lines due to columns of colloidal and molecular solutions respectively. From measurements on six substances—gold, selenium, indigo, aniline blue, indophenol, and azobenzol—he shows that, as regards light absorption, there is no real difference between colloidal solutions made up of observable discrete particles and the corresponding molecular solutions.

In an exhaustive treatment of the colours of various colloidal solutions in relation to the size of the particles, Wo. Ostwald[2] enunciates the following law: "With increasing dispersion grade (i.e. decreasing size of particles) the absorption band of any colloidal solution moves to the shorter wave-lengths". He shows that in every case observed the absorption of a colloidal solution of very high dispersion grade approximates to the absorption of the corresponding molecular solutions.

II. *Double Refraction Induced in Colloids.*—Double refraction may be induced in various solutions in the following ways:

(1) by the action of an electrostatic field (Kerr phenomenon),
(2) by mechanical action, such as stirring,
(3) by the action of a magnetic field.

The first method has been the object of much research since its discovery by Kerr[38] (see De Metz[39]). The Kerr phenomenon is shown by true molecular solutions and, therefore, may be taken as an effect produced in the molecules themselves and not on molecular complexes. Voigt ascribes the effect to the influence of the electric field on the frequency of the electrons in the liquids. In addition to this, according to Leiser, the field may produce orientation and deformation of the molecule.

The production of double refraction by mechanical means is possible only with liquids which possess a certain heterogeneity, i.e. with dispersoids of one form or another.

In the case of colloidal solutions of the ferromagnetic metals uniform magnetic fields produce double refraction. According to Cotton and Mouton,[40] this phenomenon is due to an orientation of the particles and increases in amount as the size of the particles increases (see Havelock[41]).

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CHAPTER VI.

MEASUREMENT OF THE SIZES OF ULTRAMICROSCOPIC PARTICLES.

ALTHOUGH there is no doubt that the ultramicroscope enables one to see particles much below the former microscopic limit, still there is no very rigid method by which one can measure exactly the size of the particles involved. However, there are several methods by which the approximate sizes may be determined.

Particles below the limit of visibility of the ordinary microscope have been called by Siedentopf[1] ultramicrons; if the ultramicrons are visible in the ultramicroscope, they are named submicrons; if not visible even in the ultramicroscope, amicrons. Table XVI shows the limiting sizes of the particles classed under the various heads.

TABLE XVI.—LOWER LIMITS OF DIAMETERS OF SMALL PARTICLES.[2]

Visible in ordinary microscope.	Ultramicroscopic particles.		
	Submicrons.		Amicrons.
	Electric arc illumination	Strongest sunlight	All below a diameter of
·25μμ or 2·5 × 10^{-5} cm.	15μμ or 15 × 10^{-7} cm.	1·0μμ or 1·0 × 10^{-7} cm.	1·0 × 10^{-7} cm.

It has been remarked already (p. 48) that no direct determination of the size can be made by measurement of the diameter of the particles; i.e. the ultramicroscope betrays merely the presence of the particles with practically no evidence of the dimensions or shape of the individual particles.[3] One is then forced to get at the size indirectly by determining the number of particles in a given volume and, from the known total amount of dispersed material in a given volume of the solution, to determine the mass and size of each particle.

Two methods of finding the number of particles per unit volume of solution have been used by Zsigmondy[4]:—

(1) the measurement of the average distance between neighbouring particles in a given sample of the solution;

(2) a direct count of the number of particles in a determined volume. In both of these methods the small sample viewed under the microscope must be very dilute; it is generally necessary to dilute a given colloid to some hundreds of times its original volume in order either to get the particles far enough apart for reliable measurement, or to render the number of particles few enough to be conveniently counted.

Method (1): If r equals the mean distance in cms. between the particles and if we consider them to be small spheres, then a, the radius of each sphere, is given by

$$a = \sqrt[3]{\frac{A}{d}} \, . \, r$$

where A = the weight of the particles in unit volume of the sample of the liquid viewed, and

d = the density of the particles in the sol.

Of course, in the measurement of A any dilution of the original solution must be taken into account. The values of r may be measured by means of a micrometer eye-piece or by viewing in the solution a graduated scale, such as the scale scratched on the slide of a hæmocytometer.

Method (2): Zsigmondy fixed the volume in which the number of particles was counted by means of an eye-piece micrometer and the slit S (see Fig. 4, p. 42) which bounds the illuminating pencil. "By means of the eye-piece micrometer a part of the cone of rays *dd*, Fig. 13, may be sharply defined from side to side, whereby the length and breadth of the volume chosen may be known. The depth of the illuminated volume thus defined may be easily determined with the eye-piece micrometer by a quarter rotation of the slit S."[5]

In similar observations by the author,[6] the volume of liquid viewed was determined by the use of a Zeiss hæmocytometer slide (Fig. 14). At the centre of a circular piece of glass, A, an area of 1 sq. mm. is divided into small squares of 1/20 mm. side by means of fine lines ruled with a diamond point. The plate B surrounds A so as to leave an annular trough about the central disk. The upper surface of B is exactly 0·1 mm. above that of A, so that when the cover glass C is placed on B a layer 0·1 mm. thick exists between A and C. The surfaces of A, B, and C are, of course, ground perfectly plane. When a drop of a sol is placed on A and covered with C, a volume of 0·00025 cu. mm. can be discerned through the microscope. By raising or lowering the objective very slightly, it is possible to bring all the particles in a layer 0·1 mm. thick into view, and so for sufficiently dilute solutions the number of particles per cu. mm. can be very approximately determined. The following is a sample

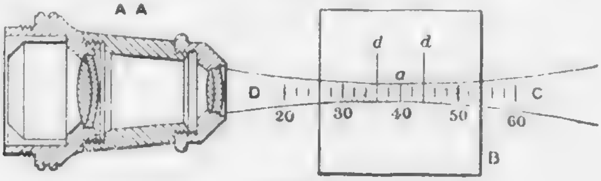

FIG. 13.

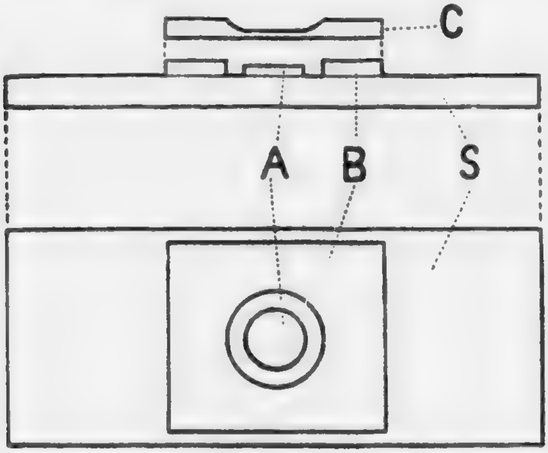

FIG. 14.

of such a determination, typical as regards the method and the magnitude of the quantities involved:—

A silver solution (after Bredig) containing 6·8 mgms. of metal per 100 ccs. was diluted with distilled water to one hundred times its original volume. A drop of the dilute liquid showed on the average the presence of 300 particles per volume 0·1 cu. mm. Therefore in the original solution per cc. there were 3×10^{8} particles weighing $6{\cdot}8 \times 10^{-5}$ grm.

If the specific gravity of the silver particles be taken as 10·5, the mean volume of the particles in solution is $2{\cdot}2 \times 10^{-14}$ cc. Assuming that the particles are in the form of small spheres, the mean radius being *a*,

$$\tfrac{4}{3}\pi a^{3} = 22 \times 10^{-15},$$
$$\therefore a = 1{\cdot}7 \times 10^{-5}.$$

There are elements of uncertainty in both of the above methods. Under the best circumstances the observations require considerable time during all of which the Brownian movement will cause particles to move into and out of the field of view; such a difficulty can be overcome only by a large number of observations on each sample. It is not known definitely whether or not merely diluting the sample may cause a change in the size of the particles. The ordinary method of finding the total amount of disperse substance per unit volume is by evaporating the solution and weighing the residue; in this, one assumes that the substance is all confined to the submicrons, while in reality there are probably always present amicrons and some of the material in the state of molecular solution. A more exact determination involves the separation of the disperse phase by means of a collodion filter and analysis of the dry residue and filtrate separately. An additional source of difficulty is in the choice of the density of the material suspended. Experiments such as those of Rose[7] and Cholodny[8] on gold and silver colloids show that there is not much error in taking the density equal to that of the solid for the metal sols; for such solutions as mastic in water, the density reckoned from the dried residue would be only an approximation.

Method (2): If the particles involved are just about the limit of the ordinary microscopic size ($1{\cdot}5 \times 10^{-5}$ cm. in diameter) the methods given by Perrin[9] (p. 82) may sometimes be used to advantage, or the size may be determined in accordance with Stokes' law by the rate of settling of the particles in the liquid. The latter gives the velocity of fall, v, of a particle of radius a through a liquid of viscosity η from the formula

$$v = \frac{F}{6\pi\eta a}.$$

F, the force acting on the particle, is in this case that due to gravity,

$$\therefore F = \tfrac{4}{3}\pi a^3(\rho - \rho_1)g,$$

where ρ and ρ_1 are the densities of the particles and the liquid medium respectively. From these equations we have

$$a^2 = \frac{9}{2} \cdot \frac{\eta v}{(\rho - \rho_1)g}.$$

The other methods[10] suggested for the determination of the radii of the particles are really of only theoretical importance. The radii may be deduced from various formulæ, such as that for the Brownian movement, which were developed for the mathematical expression of some physical property of the colloid and which involve the radii only incidentally.

In one set of formulæ of this type we may class together those which rest fundamentally on an application of Stokes' law to the equilibrium state set up in the colloidal solution, viz: (1) the formula for the Brownian movement (p. 73), (2) that expressing Perrin's law of the distribution of the particles at different heights in the liquid (p. 81), and (3) the expression for the diffusion coefficient of the particles. The latter is a result of the work of Sutherland,[11] Einstein,[12] Smoluchowski,[13] Cunningham,[14] and Millikan[15]; the diffusion constant, δ, is given by the expression

$$\delta = \frac{RT}{N} \cdot \frac{1 + A\frac{l}{a}}{6\pi\eta a},$$

where l is the mean path of the molecules of the solvent, and A is a constant of value approximately 0·815. As far as the measurement of the radius of the particle is concerned, all these methods involve work out of all proportion to their exactness and applicability.

Other suggested formulæ have to do with the optical properties enumerated in a previous chapter; for example, (1) the absorption of light by a given solution, and (2) Rayleigh's law of the scattering of light by an atmosphere of fine particles (p. 101). These phenomena involve measurements which are too indefinite to be applied to the determination of the radii of the particles.

As noted in Table XVI, the smallest particles visible in the ultramicroscope have a diameter of about 1×10^{-7} cm.; the most exhaustive work on this point is that of Zsigmondy and Siedentopf in determining the sizes of the particles in their various gold solutions. They found that even after they had deprived their solutions of all their ultramicroscopically visible particles, the solutions had still a faint opalescence and gave chemical reactions unique to the substance in solution. These facts point to the presence of amicrons and possibly molecules of gold in the solutions. On the other hand, the kinetic theory gives the following values for the sizes of the molecules named:—

hydrogen = $0{\cdot}1 \times 10^{-7}$ cm.,
methyl alcohol = $0{\cdot}5 \times 10^{-7}$ cm.,
chloroform = $0{\cdot}8 \times 10^{-7}$ cm.

In view of the small gap which exists between the largest molecule and the smallest visible submicron, it is interesting to recall the determinations of the molecular weights of some typical colloids by the methods of the depression of the freezing point and the measurement of the diffusion coefficient. As is well known, if Δ = the experimentally determined depression of the freezing point which 100 grm. of the solvent suffers through the addition of p grams of the substance, K = molecular depression of the solvent, and M = molecular weight of substance to be determined,

$$\frac{\Delta}{K} = \frac{p}{M}$$

$$\therefore M = \frac{pK}{\Delta}.$$

These determinations give the following results for the substances indicated :—

Malto-dextrine	965
Gum	1800
Glycogen	1625
Ferric hydrate	6000
Tungstic acid	1750
Egg albumen	14,000
Starch	25,000
Albumose	2400
Tannin	2643-3700

The diffusion method rests on a determination of the rate at which the colloid diffuses into pure water. If we have a solution in a trough with parallel sides and 1 sq. cm. cross-section and the solution at one plane perpendicular to the column of liquid is $(n + \frac{1}{2})$ normal and that at a second plane, 1 cm. from the former and parallel to it, is $(n - \frac{1}{2})$ normal, then the difference in osmotic pressure at the two planes is equal to the osmotic pressure of a normal solution,

$$= RT \text{ per sq. cm. at } 0^\circ \text{ C.}$$

This pressure tends to drive the dissolved molecules in the direction of the lower concentration, and acts on all dissolved molecules between the two planes perpendicular to the liquid, i.e. on $\frac{n}{1000}$ grm.-molecules. If the force necessary to drive 1 grm.-molecule of the dissolved substance with a velocity of 1 cm. per sec. is P kilograms—this force is known as the coefficient of friction of the substance—the velocity v is given by

$$v = \frac{RT \cdot 1000}{1000\,P \cdot n} \text{ cms. per sec.}$$

The quantity of dissolved substance passing the plane of lower concentration in 1 sec. is found from the number of molecules lying between that plane and a parallel plane v cms distant.

The number of milligram-molecules in the volume v ccs. is $v \times n = K$,

$$\therefore K = \frac{R \cdot T}{P}.$$

K is called the diffusion coefficient.

The friction coefficients of substances of non-conducting solutions are found from the diffusion coefficient. According to a calculation made by Euler the friction of a gram-molecule is approximately proportional to the square root of the molecular weight of the dissolved substance. If we apply this method to calculate the molecular weight of the four colloids examined by Graham, we have:

Gum arabic	= 1750
Tannic acid	= 2730
Egg albumen	= 7420
Caramel	= 13,200

These determinations offer strong evidence of the continuous gradation in the sizes of the particles of the disperse phase of various solutions, from the size of ordinary molecules to that of the particles of coarse suspensions.

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CHAPTER VII.

MOTIONS OF PARTICLES IN AN ELECTRIC FIELD.

1. *Cationic and anionic solutions.*—The investigation of this property of the so-called colloidal solutions dates from the work of Linder and Picton.[1] Prior to that, experiments on the motion of the particles of ordinary suspensions under an electric field had been carried out by various workers, and briefly the results obtained were as follows[2]:—

In suspension in water, the particles of starch, platinum black, finely divided gold, copper, iron, graphite, quartz, feldspar, amber, sulphur, shellac, silk, cotton, lycopodium, paper, porcelain, earth, and asbestos, move towards the positive pole.

When the above materials are suspended in a similar manner in turpentine oil, they all move towards the negative pole, with the sole exception of sulphur, which moves in the same direction in turpentine as in water.

Fine gas bubbles of hydrogen, oxygen, air, ethylene, carbon dioxide, and small liquid globules of turpentine and carbon bisulphide, when in water, all move toward the positive pole."

Turpentine globules and small gas bubbles in ethyl alcohol move to the positive pole.

Quartz particles and air bubbles in carbon bisulphide move to the negative pole.

These results led Wiedemann to make the statement that "in water all bodies appear, through contact, to become negatively charged, while, through rubbing against different bodies, the water becomes positively charged".

When Linder and Picton tested similar properties of the particles in chemically prepared solutions, they found that such a generalization was inexact. They give the following results:—

Suspensions of aniline blue, arsenic sulphide, indigo, iodine, shellac, silicic acid, starch and sulphur in water, and of bromine in alcohol, show attraction to the positive electrode.

The following materials suspended in water move in the opposite direction: Ferric hydrate, hæmoglobin, Hoffman's violet, Magdala red, methyl violet and rosaniline hydrochloride.

As a conclusion to their work Linder and Picton make the significant statement that experiment seems to show that, if the solution is basic or tends to break up so as to leave a free base active, the motion is to the negative pole, i.e. the particle is positively charged; if the solution is acidic, motion is to the positive pole, and consequently the particles are negatively charged.

Taking into consideration the recent results of many workers, we may divide colloidal solutions and suspensions into two classes, anionic and cationic, according as the particles in solution move to the anode, i.e. are negatively charged, or to the cathode, i.e. are positively charged (p. 22).

Solutions in water:—

Anionic.

1. The sulphides of arsenic, antimony, and cadmium.
2. Solutions of platinum, silver, gold, and mercury.
3. Vanadium pentoxide.
4. Stannic acid and silicic acid.
5. Aniline blue, indigo, molybdena blue, soluble Prussian blue, eosin, fuchsin.
6. Iodine, sulphur, selenium, shellac, resin.
7. Starch, mastic, caramel, lecithin, chloroform.
8. Silver halides.
9. Various oil emulsions.

Cationic.

1. The hydrates of iron, chromium, aluminium, copper, zirconium, cerium, and thorium.
2. Bredig solutions of bismuth, lead, iron, copper.
3. Hofmann violet, Magdala red, methyl violet, rosaniline hydrochloride, Bismarck brown, methylene blue.
4. Albumen, hæmoglobin, agar.
5. Titanic acid

The charges on particles of starch, gelatine, agar, and silicic acid are very small and difficult to observe.

Bredig solutions[3] of lead, tin, and zinc in ethyl alcohol are all cationic, while bromine in the same solvent is anionic. Methyl alcohol gives Bredig solutions with lead, bismuth, iron, copper, tin, and zinc which are cationic. The writer has also prepared anionic solutions of platinum, silver, and gold in ethyl malonate by Bredig's method.

According to Thornton[4] diatoms, unicellular algæ, and vegetable micro-organisms in general are positively charged (cationic solutions) and amœbe and animal micro-organisms in general are negatively charged (anionic solutions) (see also Schneckenberg[5]).

Some organic colloids, such as globulin, and some inorganic, such as silicic acid, are anionic in alkaline solution and cationic in acid solution.

2. *Theory of cataphoresis.*—The study of the electrical motion of particles in suspension follows the work of Reuss, Faraday, Wiedemann, and Quincke on the phenomenon of electrical osmosis. When the anode and cathode compartments of a conductivity tube are separated by a diaphragm of porous earthenware, the electrolyte will pass through this wall towards the cathode until an equilibrium pressure is attained. Similar effects were found by Quincke[6] by using capillary tubes instead of the earthenware diaphragm. The liquid was varied and the influence of the surface of the capillary was tested by lining the glass tube with other substances, e.g. sulphur; oil of turpentine flowed toward the anode through a glass tube, but toward the cathode when the glass capillary was lined with sulphur. The interstices between the particles, suspended in a liquid and set in motion by an electric field, may be looked upon as, in effect, a series of movable capillary walls; that is, the liquid is stationary while the walls themselves (the particles) move in the field.

The theory of this motion of finely divided particles in suspension in liquids was long since propounded by Helmholtz[7] and later amplified by Lamb.[8] Without assuming, for the moment, anything with regard to the cause of the formation of the colloidal solutions, we may apply the same theoretical considerations to the movements of these particles.

The fundamental assumption is that when a particle suspended in a liquid becomes charged, there exists about it a double electric layer; when the particle is negatively charged, there is a layer of negative electricity on the surface of the solid particle, while in the liquid immediately surrounding it there is a corresponding layer of positive electricity. "On the whole the algebraic sum of the two equals zero, and the centre of gravity of the complete system, solid particle and surrounding positively charged fluid layer taken together, cannot be moved by the electric forces which arise from the potential fall in the liquid through which the current passes. However, the electric force will tend to bring about a displacement, relatively to each other, of the positively charged fluid layer and the negatively charged particle, whereby the fluid layer follows the flow of positive electricity while the particle moves in the opposite direction. If the liquid were a perfect insulator the new position would still be a condition of equilibrium. Since, however, through the displacement of the layers the equilibrium of the galvanic tension between the solid particle and the liquid is disturbed, and on account of the conductivity of the liquid always seeks to restore itself, the original state of electrical distribution will tend to be continually reproduced and so new displacements of the particle with respect to the surrounding liquid will continually occur."[2]

This theory was put forward by Helmholtz in the course of his mathematical development of the explanation (suggested by Quincke) of the electrical transport of conducting liquids through the walls of porous vessels or along capillary tubes; Quincke assumed that there existed a contact difference of potential between the fluid and its solid boundaries. Throughout his treatment of the phenomenon, Helmholtz considers that there is no slipping of the fluid over the surface of the solids with which it is in contact. On this point Lamb disagrees with Helmholtz, holding that the solid offers a very great, but not an infinite, resistance to the sliding of the fluid over it, and that, while the effect of this slipping would be entirely insensible in such experiments as those of Poiseuille, it leads to appreciable results in the present case in consequence of the relatively enormous electrical forces acting on the superficial film of the liquid and dragging the fluid, as it were, by the skin through the tube. The practical difference between the views taken by Helmholtz and Lamb respectively may be shown in a simple case. Using the numerical results found by Wiedemann, Helmholtz infers that for a certain solution of copper sulphate in contact with the material of a porous clay vessel, the contact difference of potential E between the solution and the solid wall is given by

$$\frac{E}{D} = 1{\cdot}77$$

where D is the electromotive force of a Daniell's cell. The variation introduced by Lamb would change this equation into

$$\frac{E}{D} \cdot \frac{l}{d} = 1{\cdot}77 \quad . \quad . \quad . \quad . \quad (1)$$

where d = the distance between the plates of an air condenser equivalent to that virtually formed by the opposed surfaces of solid and liquid, and l is a linear magnitude, measuring the "facility of slipping" and equal to η/β, η being coefficient of viscosity of the liquid and β the coefficient of sliding friction of the fluid in contact with the wall of the tube. Lamb gives reasons for supposing that l and d are of the same order of magnitude (that of 10^{-8} cm.). Of course if $l = d$, Helmholtz's formula remains unchanged, and it is very probable that the ratio $\frac{l}{d}$ differs very little from unity.

Lamb deduces the following expression for the velocity (v) of a charged particle through a liquid under an electric force, when the motion has become steady:—

$$Xe = 4\pi a^2 . \eta . v \frac{1}{l} \quad . \quad . \quad . \quad . \quad (2$$

where X = gradient of electric potential in the liquid,
e = charge on the particle,
a = radius of the particle,
and η and l as above.

We may look upon the particle with the double electric layer as a small condenser of two concentric spheres whose distance apart (d, the same as before) is small compared with a.

The capacity of such a condenser would then be given by

$$C = \frac{a^2}{d} K \quad . \quad . \quad . \quad . \quad (3)$$

where K = specific inductive capacity of the liquid.

If V indicates the contact difference of potential between the solid and the liquid, we have (since Q = CV),

$$e = V \frac{a^2}{d} K \quad . \quad . \quad . \quad . \quad (4)$$

Substituting this value of e in equation (2) and transposing we get

$$V . \frac{l}{d} = \frac{4\pi}{K} . \frac{\eta v}{X} \quad . \quad . \quad . \quad . \quad (5)$$

all electrical measurements being made in electrostatic units.

This equation, which is similar to one given by Perrin,[10] will enable us to find values of $V . \frac{l}{d}$ for any solid and liquid, if for known values of X, we can observe the corresponding values of v.

We may deduce immediately from this formula that the mobility of a particle of given constitution, in a given liquid medium, is independent of the radius, and that the product ηv for a given solution must be constant.

3. *Method of measuring the velocities of particles* (in cms. per sec. for field of potential gradient equal to one volt per cm.).—Two methods have been used for measuring the velocity of colloidal particles: (1) the **U**-tube method due to Nernst, Whetham, and Hardy,[11] and (2) the ultramicroscopic observation of the velocity of single particles in an electric field.

Probably the first is the more reliable method of the two. The limbs of the **U**-tube used by the writer [12] were each about 12 cms. long and about 1·5 cms. in diameter (Fig. 15); they were graduated in mms. throughout their length. Into the bottom of the **U**-tube is sealed a fine delivery tube provided with a tap (T) and a funnel (F); this tube is bent round so as to run up behind the limbs and to bring the funnel to the same height as the top of the **U**-tube.

The colloidal solution to be tried is poured into the funnel so as to fill the funnel and small tube to the tap, which is closed; water having a specific conductivity equal to that of the colloid is then poured into the **U**-tube so as to fill it to a height of about 3 cms. The whole tube is then placed in a large glass water bath so as to be almost submerged; this water should be kept at a constant temperature during the course of any experiment. At the end of a few minutes the tap (T) is opened very slightly and the colloidal solution allowed to force the water gently up the limbs of the tube to any required height. If carefully manipulated the surface of separation between the clear water and the solution is very distinct and will remain so for hours. Two electrodes of coiled platinized platinum foil are supported at a convenient level in the two limbs of the tube and the clear water allowed to rise well above them. The electrodes are attached to the terminals of a set of storage cells of constant voltage, and when the current is completed the surface of separation in one limb will at once begin to rise gradually while that in the other will sink. In practice, the connexions may be made through a reversing key and the voltage, usually fixed at about 110 volts, may be left on one way for ten minutes and then reversed for twenty minutes. The velocity is reckoned from the displacement of the surfaces during this final twenty minutes; one-half the sum of the displacements in the two tubes is taken as the distance travelled by a particle in the given time. A typical set of observations is given in Table XVII.

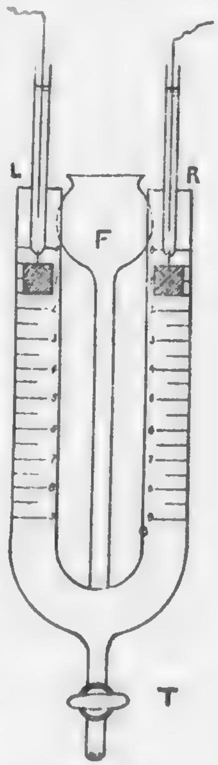

FIG. 15.

TABLE XVII.

Time.	Voltage—Sign of Right Electrode.	Temp.	Height of Colloidal Surface.		Observed Velocity in cm./sec.
			Left.	Right.	
11·37	+ 118	11° C.	54 mms.	55 mms.	
11·47	+ 118		61 „	50 „	
Current	off				
11·48	− 118	11° C.	61 „	50 „	
11·58	− 118		55 „	56 „	96 × 10
12·08	− 118	11° C.	50 „	62 „	

Electrodes at 15 mms. in each limb.

It will be seen from the table that there has been an apparent settling of the colloid in the tube while the current was running. This is quite usual but, as the reckoning is made, it could not affect the rate, since this slight lowering of the surface is uniform in both limbs, so that while it is added to the velocity in one limb it is subtracted from the velocity in the other.

In order to find the value of the electric force in the tube, it is of course necessary to know the effective distance between the electrodes A and B. To do this the tube is filled with, say, a ·01 normal potassium chloride solution, placed in the water bath, and the resistances are taken with the electrodes placed at the successive centimetre marks down the tube. In this way, for the particular tube used for the above results, it was found that the resistance of the curved part of the tube from 90 in L to 90 in R was 8·8 times the resistance of each cm. length of the single limbs. So that when, as in the case cited in Table XVII, the electrodes were placed at 1·5 in each tube, the effective distance between the electrodes was 23·8 cms. and therefore the strength of the electric field was $\frac{118}{23·8} = 4·9$ volts per cm. Thus the absolute value of the mobility of the silver particles in water at a temperature of 11° C. would be $19·6 \times 10^{-5}$ cm. per sec. per volt per cm.

In order to obtain dependable results, great care must be taken to have the temperature of the colloidal solution and the supernatant liquid quite uniform before the tap T is first opened and throughout the whole of the observation; the whole tube should be kept in a water bath during all this time.

A method similar to the above was used by Coehn[13] and by Galecki[14] in similar measurements.

Whitney and Blake[15] and Schmauss[16] measured the velocities of colloidal particles by immersing the electrodes in the colloidal solution itself. This method has two disturbing elements; in the first place, the products of electrolysis produced at the electrodes affect immediately the solution itself and, in the second place, there occurs at the electrodes a charging and discharging of the particles which causes anomalous motions in the neighbourhood of the electrodes.[17]

The first workers to use the ultramicroscope for velocity measurements were Cotton and Mouton.[18] Electrodes were introduced, a few mms. apart, into the sample of solution contained in the microscopic slide, a difference of potential of a few volts applied, and the time required by a single particle to cross the field of view noted. They found that as long as they viewed only the particles in the middle of the layer, the results were concordant, but as the particles in view were situated nearer and nearer to the bottom or to the top of the cavity, the motion of the charged particles first ceased and then was reversed. The distance from the glass walls to the layer at which reversal took place was 25μ. Cotton and Mouton found that this reversal took place both with negatively and with positively charged particles. Near the walls of the chamber one would expect the liquid to move toward the cathode and sweep the particles along with it; it is difficult to explain, however, the reversal of the motion in the case of the positively charged particles.

In working with oil emulsions by this method, Ellis[19] introduced corrections for this disturbing feature by observing the apparent velocity at given depths and calculating the probable value of the velocity of the particles relatively to the liquid. In addition to the action of endosmose, there are inherent in this method the same difficulties as indicated above in the Whitney and Blake method: viz. the disturbances due to the electrodes being introduced directly in contact with the colloid itself.

It was suggested by Ellis that endosmose affects the results in the **U**-tube method, but in the author's experiments tubes of various sizes have been used at different times and all gave concordant results. Recent work by McTaggart[20] on the measurement of similar velocities for air bubbles in various liquid media shows that there is no such effect for tubes with diameters of the order of one or two cms.; further, such an effect would be extremely small for the small currents used in such experiments.

4. *Experimental values of the mobilities of particles.*—In Table XVIII are collected the experimental determinations of the mobilities of particles in suspension; the results are expressed in cms. per sec. per volt per cm. The prefixed sign indicates the kind of charge possessed by the particles.

In the last column of the table on opposite page are given the values of the potential difference between the particle and the medium, as calculated from the formula, p. 130 (*l – d*). The corresponding values obtained by Quincke[6] and Tereschin[26] for the potential difference between glass and water in endosmose experiments were respectively ·053 and ·047 volt; Schmoluchowski[27] points out that this means that glass particles in water (at 18° C.) would move in an electric field of one volt per cm. with the velocity of 34×10^{-5} cm. per second—a value in close agreement with many of the mobilities in the table. This agreement is more than a coincidence and suggests that a common cause must account for the charging of the particles in the various cases.

On the other hand, at the bottom of the table are inserted the values of the corresponding mobilities of typical electrolytic ions in dilute solutions. Keeping in mind that Stokes' law (see Cunningham[28] and Millikan[29]) does not hold in its ordinary form when the radii of the particles approach the length of the mean free path of the molecules of the medium, we may consider that there is a possibility of complete continuity in this phenomenon of motion in an electric field as

TABLE XVIII.—MOBILITIES OF THE DISPERSE PHASE IN VARIOUS AQUEOUS SOLUTIONS.

Disperse phase.	Mobility in cms. per sec. per volt per cm. × 10^{-5}.	P.D. in volts between the disperse phase and medium.	Author
Suspensions.			
Lycopodium	– 25·0	– ·035	Quincke [6]
Quartz	– 30·0	– ·042	Whitney and Blake [15]
Air bubbles	– 40·0	·056	McTaggart [20]
Suspensoids.			
Arsenious sulphide	– 22·0	– ·031	Linder and Picton [1]
Prussian blue	– 40·0	– ·056	Whitney and Blake [15]
Prussian blue	– 41·5	– ·058	Burton [21]
Gold (chem. prep.)	– 40·0	– ·056	Whitney and Blake [15]
Gold (chem. prep.)	– 7·1 to 57·4		Galecki [14]
Gold (chem. prep. and Bredig)	– 26·0	– ·036	Rolla [22]
Gold (Bredig)	– 21·6	– ·030	Burton [18]
Platinum	– 30·0	– ·042	Whitney and Blake [15]
Platinum (Bredig)	– 24·0	– ·034	Rolla [22]
Platinum (Bredig)	– 20·3	– ·028	Burton [12]
Platinum (Bredig)	– 20 to 40		Svedberg [23]
Silver (Bredig)	– 32·0 to 38		Cotton and Mouton [16]
Silver (Bredig)	– 20·0	– ·028	Svedberg [23]
Mercury (Bredig)	– 25·0	– ·035	Burton [12]
Silver (Bredig)	– 23·6	– ·033	"
Bismuth (Bredig)	11·0	·015	"
Lead (Bredig)	12·0	·017	"
Iron (Bredig)	19·0	·027	"
Ferric hydroxide	30·0	·042	Whitney and Blake [1]
Ferric hydroxide	52·5	·073	Burton [21]
HA Globulin	– 19·8 to 22·9	– ·031	Hardy [24]
HCl Globulin	– 9·0 to 11·5	– ·015	"
NaOH Globulin	7·7	·010	"
H_2SO_4 Globulin	– 18·5	– ·026	"
H_3PO_4 Globulin	– 23·0	– ·032	"
Emulsions.			
Hydrocarbon oil	– 43·0	– ·060	Lewis [2]
Spec. acid-free oil	– 37·2	– ·052	Ellis [19]
Acid-free oil	– 32·4	– ·045	"
Liquid paraffin	– 29·3	– ·041	"
Cylinder oil	– 27·0	– ·038	"
Water-soluble oil	– 48·0	– ·067	"
Aniline, fresh dist.	– 31·1	– ·043	"
Chloroform	– 10·0	– ·014	"
Gummigutt	– 18·1	– ·025	"
Mastixharz	– 17·7	– ·024	"
Electrolytic ions.			
Organic Comp.'s (high mol. wt.)	20·0		
Hydrogen (+)	320·0		
Hydroxide (–)	180·0		
Chlorine (–)	68·0		

we go from suspensions of large particles through the region of ordinary colloidal solutions to true solutions.

As we shall see later, the mobility possessed by such particles is greatly affected by the introduction of extremely small traces of electrolytes and, consequently, one gets some variety in the values of the mobility, obtained when the specific conductivity changes. For example, copper solutions, the specific conductivity of which varied from $3{\cdot}1 \times 10^{-6}$ to $8{\cdot}2 \times 10^{-6}$, gave mobilities varying from $33{\cdot}0 \times 10^{-5}$ to $23{\cdot}4 \times 10^{-5}$ cm. per sec. per volt per cm. It is impossible, therefore, to assign a definite number as the transport number of a particular colloidal particle.

We have already noted (p. 130) that the mobility of a particle of given constitution in a given liquid medium is independent of the size of the particle. Hardy[illegible] prepared a series of similar sols of globulin containing particles of different sizes, but found that the velocities with which they moved in a given electric field were always the same. If particles of different sizes do exist in the electrically prepared solutions, the size would probably depend on the violence of the sparking during the preparation of the solution. Three silver solutions were prepared by the writer by using varying currents and voltages for producing the spark, all other conditions being the same except the time of sparking. As shown in Table XIX, the differences in the mobilities, which were all determined at 11° C., are all within the limits of error in the experiment.

TABLE XIX.—SILVER SOLUTIONS.

No.	Voltage.	Current.	Time of sparking.	Mobility in [illegible] per volt per [illegible]
1	80 volts.	8·5 amperes.	10 mins.	$-19{\cdot}7 \times 10$[illegible]
2	60 ,,	7·5 ,,	20 ,,	$-19{\cdot}6 \times 10$[illegible]
3	[illegible] ,,	6·5 ,,	30 ,,	$-19{\cdot}3 \times 10$[illegible]

Since there is no *a priori* reason for assuming that all the particles are of a uniform size, these results would confirm Lamb's theory.

5. *Effect of Concentration of Solution.*—The writer has carried

out a series of experiments on the validity of the formula given on page 130 in so far as ηv = constant, as long as one deals with the same material in the particle, the same liquid medium, and constant potential gradient.

TABLE XX.—SILVER COLLOIDAL SOLUTIONS.

No.	Temperature Centigrade.	Mobility (v).	Viscosity of water at given temperature η.	Product ηv
1	3°	$15{\cdot}1 \times 10^{-5}$	·016214	$24{\cdot}5 \times 10^{-7}$
2	9·9°	$18{\cdot}6 \times 10^{-5}$	·013300	$24{\cdot}7 \times 10^{-7}$
3	11°	$19{\cdot}6 \times 10^{-5}$	·012822	$25{\cdot}1 \times 10^{-7}$
4	21°	$25{\cdot}5 \times 10^{-5}$	·009922	$25{\cdot}0 \times 10^{-7}$
5	31°	$30{\cdot}1 \times 10^{-5}$	·007972	$24{\cdot}0 \times 10^{-7}$
6	40·5°	$37{\cdot}2 \times 10^{-5}$	·006577	$24{\cdot}5 \times 10^{-7}$

In Table XX are given the mobility determinations for silver colloidal solution in water over a range of temperatures from 3° C. to 40·5° C. In performing these experiments the water bath in which the velocity tube was always supported was heated and the water constantly stirred; the temperature was maintained constant at any one time by the use of an ordinary thermostat. The sensibly constant value of ηv is in good accord with the requirements of the velocity formula.

These experiments also indicate the primary importance of taking account of the temperature in this work; a neglect of the influence of changing temperature in any form of apparatus for measuring these velocities leads to bewildering results.[17]

6. *The effect of the medium.*—Linder and Picton[1] first suggested some interaction between the liquid medium and the particles: "Experiment seems to show that if a solution is basic or tends to break up so as to leave a free base active, the motion is to the negative pole. If the solution is acidic (or tends to break up so as to leave a free H ion active) motion is to the positive pole."

On account of the inadequacy of a purely physical explanation of the cause of the charge possessed by colloidal particles, Hardy[21] was led to account for the phenomena from a chemical point of view. In the samples of globulin tabulated on

p. 135 acid globulin gives cationic solutions, while basic globulin gives anionic solutions.

A consideration of the classification of the Bredig metallic hydrosols and alcosols, given on page 126, sheds light on the influence of the medium. In the results given in Table XVIII one is struck with the fact that the particles of the electro-positive oxidizable metals are all positively charged, while the electro-negative non-oxidizable metals give negatively charged particles. When we recall that the iron in such solutions appears to form the hydrate, and that the particles bear a charge of the same sign as the particles in chemically prepared colloidal solutions of ferric hydrate, one is justified in suspecting that in the cases of iron, bismuth, lead and copper the process of manufacture of these electrically prepared solutions involves the production of a certain amount of the hydrate of the metal. Such an hypothesis at once suggests an analogous action on the part of gold, silver, platinum, and mercury, viz. an interaction between the metal and hydrogen—a view to which the already known existence of a hydride of platinum would lend some colour.

This explanation was first offered by Hardy[31]: "Consider the hydrosol of a metal such as platinum. The colloid particles are negatively charged, they are anionic in character, and the charge is due to a reaction between the metal and the water at the moment of formation of the hydrosol whereby the hydride $\mathrm{P}t\mathrm{H}$ is formed which ionizes in the sense

$$\mathrm{P}t\mathrm{H} \rightleftarrows \mathrm{P}t' + \mathrm{H}^{\cdot}.$$

The chief number of the ions $\mathrm{P}t'$ are in the form of masses so large as to have the properties of matter in mass, they are not of molecular dimensions and they form an internal phase. Ionization is a phenomenon of the surface of these masses only. It confers on the particle its electrical charge, and it is in this case the 'incomplete chemical combination' which Lord Rayleigh regards as the source of contact differences of potential to which I referred in an earlier paper. In reactions therefore an electropositive colloid is a weak alkali, e.g. hydrosol of ferric hydroxide, and an electronegative colloid a weak acid, e.g. silica."

The suggestions given by these results for the hydrosols are strengthened by the observations on colloidal solutions in the alcohols, which we may call, after Graham, alcosols. Pure methyl alcohol and pure ethyl acohol were used in the preparation instead of water.

Although repeated trials were made with the metals gold, silver, and platinum, the writer has never succeeded in getting them to remain suspended in either of these alcohols. On the other hand, the metals lead, tin, and zinc form solutions in both of the alcohols, while with methyl alcohol solutions were also obtained with bismuth, iron, and copper. In all these solutions the particles moved to the negative electrode in an electric field, i.e. they are positively charged.

Viewing these results in the light of the chemical nature of the alcohols, the former suggestion as to the interaction between the liquid medium and the metals is strengthened. Although these alcohols have a neutral reaction, they act like weak bases in combining with acids to form salts, or, in other words, they have an easily replaceable OH group. The easily oxidizable metals would thus be able to form at least a surface coat of hydrate, while the metals gold, platinum, and silver, the existence of which in a colloidal state depends on a replaceable hydrogen in the liquid, cannot form in the alcohols.

A still further test of this hypothesis is afforded when one uses as the liquid medium a substance which has a replaceable H and not an OH. Anhydrous acids might be used, but there is great difficulty in keeping them free from water and, as is well known, electrolytes containing acids have extremely strong power of coagulating solutions. Ethyl malonate (Spence [4]) is a liquid which fulfils the condition of having a replaceable H. When platinum, gold, and silver were sparked underneath this liquid, very stable colloidal solutions were obtained; those of the first two metals named are apparently as stable as the corresponding hydrosols, while the gold solution coagulates at the end of a month or so. These particles were all found to bear a negative charge, similar to those of platinum, silver, and gold in hydrosols. When the other metals, bismuth, lead, zinc, and iron, were used, a colloidal solution in ethyl malonate could not be obtained.

On sparking with silver electrodes in pure anhydrous ether, $(C_2H_5)_2O$, a colloidal solution was obtained, the particles of which possess a negative charge as shown by a slight motion under the influence of an electric field. Lead electrodes did not give a colloidal solution in ether.

In the accompanying table are given the values of the potential differences between the particles and the medium for the solutions in the alcohols and ethyl malonate in comparison with the hydrosols.

TABLE XXI.—VALUES OF V IN VOLTS.

Metals.	In water K = 80.	In ethyl malonate K = 10·6.	In ethyl alcohol K = 25·8.	In methyl alcohol K [illegible]
Platinum . . .	− ·031	− ·054		—
Gold	− ·033	− ·033		
Silver . . .	− ·036	− ·040		
Lead	+ ·018	—	+ ·023	+ ·044
Bismuth . . .	+ ·017	—	—	+ ·022

This table shows a surprisingly close agreement among the differences of potential between the particles and the liquids. Taking into account the wide differences between the specific inductive capacity, say, for water and ethyl malonate, we can deduce that the charge of electricity on the particle of a given metal must be much greater in water than in ethyl malonate; in other words, the interaction between the particle and the solvent seems to be dependent on what may be defined as the ionizing power of the liquid. It is further interesting to note that these values for the differences of potential between the particles and the liquids are of the same order as the value found by Perrin for the difference of potential between chromium chloride diaphragm and slightly acidulated water (·025 volt), and also agrees in the same way with Helmholtz's values for the difference of potential between very dilute aqueous solutions and the walls of glass tubes in which they were contained, if the corrections are made by introducing the value for the specific inductive capacity of water.

7. *Theoretical considerations.*—There is practically unanimity in the opinion that these particles in colloidal solutions are inclosed by a double electric layer, the electricity of one sign on the surface of the particle being in equilibrium with an equal amount of electricity in the layer of liquid immediately surrounding the particle. It is a matter of doubt how this double layer is formed.

Following the opinion given by Quincke regarding suspensions of microscopic particles in liquids, many writers have been content to view the phenomena as an effect expressed by the term "contact electrification"; the particles become charged by the rubbing of the moving particles of the liquid itself against the suspended particles.

The recent work of Perrin[20] has produced results which throw considerable light on the phenomena of electrification by contact between liquids and solids. By measurements of the electric osmose of liquids through diaphragms of various materials he is led to these two laws:—

1. Electric osmose is only appreciable with ionizing liquids; or, in other words, ionizing liquids are the only ones which give strong electrification by contact.

2. In the absence of polyvalent radicals, all non-metallic substances become positive in liquids which are acidic, and negative in liquids which are basic.

In explaining these results he suggests the hypothesis that a positive electrification of a wall bathed by an acidic liquid is formed by H ions situated in the stationary liquid layer immediately contiguous to the wall. Opposed to it at a small distance there will be a corresponding excess of negative ions forming another layer. When the wall assumes a negative charge it is on account of similar action of the OH ions. It is found that H and OH ions move much more quickly than other ions; if then we explain this high velocity by assuming that they are smaller than other ions, we should expect them to penetrate nearer to the boundary of the liquid and so muster at the limiting layer of a liquid an excess of electric charges of one sign. Although the analogies between this phenomenon of electric osmose and that of the coagulation of colloidal solutions undoubtedly help in explaining the latter, the formation of these solutions can hardly be credited to merely physical diffusion of the H and OH ions. As we have seen from the sign of charges borne by particles in solution, it is those which appear to depend on a replaceable H which are negative, while those depending on a replaceable OH are positive.

The two views are given thus by Noyes[33] :—

"In regard to the cause and character of the electrification two assumptions deserve consideration; one, that it is simply an example of contact electricity, the colloid particle assuming a charge of one sign and the surrounding water one of the other. This correlates the phenomena of migration with that of electric endosmose. It does not, however, give an obvious explanation of the facts that the basic colloidal particles become positively charged and the acidic and neutral ones negatively charged. The other assumption accounts for these facts. According to it the phenomenon is simply one of ionization. Thus each aggregate of ferric hydroxide molecules may dissociate into one or more ordinary hydroxyl ions and a residual positively charged colloidal particle, and each aggregate of silicic or stannic acid molecules into one or more hydrogen ions and a residual negatively charged colloidal particle. . . . To explain the behaviour of neutral substances like gold or quartz by this hypothesis, it is necessary to supplement it by the assumption that in these cases it is the water or other electrolyte combined with or absorbed by the colloidal particles which undergoes ionization. It seems not improbable that there may be truth in each of these hypotheses, contact electrification occurring in the case of the coarse suspensions and ionization in the case of those which approximate more nearly to colloidal solutions."

Comparing the results given for the signs of the charges borne by the particles in different solutions, we have the following :—

1. Water ($H^+ . OH^-$) can form two classes of colloids, the particles of which are respectively positively and negatively charged.

2. Replacing the mobile H^+ by the groups C_2H_5 and CH_3, to form the alcohols, seems to destroy the power of forming solutions with negatively charged particles.

3. Ethyl malonate $CH_2(COOC_2H_5)_2$, which has the mobile H, readily forms those solutions containing the negatively charged particles and those only.

It is evident that the formation of the solution depends on the chemical nature of the solvent. This leads to the following theory of the constitution of the solution:

(1) In the case of gold, silver, and platinum in water or ethyl malonate, we have an incomplete chemical combination with the liquid; thus for platinum and water we have the equation

$$n\,Pt + H^+ . OH^- = (Pt_n H^+) + OH.$$

In analogy with Nernst's hypothesis of the solution pressure of metals in contact with an electrolyte, we may look upon the platinum-hydrogen aggregate as dissociating slightly so as to form an atmosphere of positively charged hydrogen ions about the negatively charged colloidal particle.

(2) With the other metals in water or the alcohols, we have a corresponding formation of the hydroxide, thus

$$n . Pb + H^+ . OH^- = (Pb_n . OH^-) + H.$$

By slight dissociation of the aggregate $(Pb_n . OH)$ we obtain a positively charged colloidal particle surrounded by a layer of OH^- ions in the liquid.

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CHAPTER VIII.

COAGULATION OF COLLOIDS.

I. BY ELECTROLYTES.

FOR several years experiments have been carried out on the coagulating power of electrolytes added to colloidal solutions. Scheerer[1] (1852) found that turbid aqueous solutions of whatever chemical nature were clarified by the addition of strong acids or one of the salts of a strong acid. Faraday[2] (1856) noticed that his chemically prepared gold solutions changed colour on the addition of salt—a phenomenon which he correctly ascribed to an increase in the size of the particles. Crum[3] (1854) found that the acid or salt necessary to coagulate colloidal aluminium hydroxide was absorbed by the precipitate. When Graham[4] first discussed the division of materials into crystalloids and colloids he noted as one of the important characteristics of colloids their relation to added crystalloidal electrolytic solutions. He says: "The colloid, although often dissolved in a large proportion by its solvent, is held in solution by a singularly feeble force. Hence colloids are generally displaced or precipitated by the addition to their solution of any substance from the other class." About the year 1868, Jevons[5] completed his microscopic experiments on the Brownian movement of particles in suspensions; he observed that this movement existed parallel with the stability of the suspension. The addition of acids, alkalies or salts, independently of their chemical constitution, caused the cessation of the Brownian movement and coagulated the suspensions. These results led Jevons to suggest that the particles were electrically charged. This microscopic work was carried further by Gouy[6] (see chap. IV.). Stingl and Morawski[7]

(1879) observed in a sulphur sol under the microscope small round bodies which they took to be bubbles filled with water. They believed that the addition of a salt solution caused diffusion of the salt into the bubbles and, as a consequence, destroyed the motion; the stopping of the motion allowed the bubbles to unite into larger complexes which were then drawn to the bottom of the vessel.

These early researches really open up all the questions which modern work has tried to answer: viz. the powers of various electrolytes to coagulate different colloidal solutions, the relation of the addition of the electrolyte to the charge on the particles and to the surface tension between the particle and the medium, the details of the process by which the particles unite to form the coagulum as revealed by the microscope and by the colour changes of the sol, the effect of the absorption by the coagulum of part of the electrolyte added, and the relation of hydrolysis and chemical combination to the coagulative action.

We shall discuss the influence of added electrolytes under the following heads:—

(1) Coagulative powers as determined experimentally by precipitation;

(2) Electrokinetic effects and the theory of the isoelectric point;

(3) Parallel action of electrolytes in electro-endosmose phenomena;

(4) Direct observation of the effects by the ultramicroscope;

(5) Changes caused in the physical properties, e.g. colour, viscosity;

(6) The function of the portion of the salt entrained by the coagulum.

As already pointed out in chapter II. the separation of colloidal solutions into suspensoids and emulsoids is markedly justified by wide differences in sensitiveness to added electrolytes. As a general rule, suspensoids are precipitated by extremely small additions of electrolytes, while the emulsoids are affected by comparatively strong solutions only. Relatively little work has been done on the latter class: according to Spiro, the precipitation of emulsoids "can be adequately explained as a separation into two phases, one a solid phase rich in the colloid, poor in salt and water, the other a fluid phase, rich in water and salt, poor in the colloid, the action being exactly similar to the salting out of alcohol from a mixture of alcohol and water by the addition of magnesium carbonate.

"Electrical precipitation is distinguished from salting out in the same way as is the precipitation of calcium from a solution of the hydroxide by potassium sulphate to the precipitation of potassium sulphate by calcium sulphate as the double salt $K_2SO_4 . CaSO_4 . 4H_2O$. In the one case the precipitant is decomposed, in the other case it is not. The precipitation of electrically active hydrosols is distinguished also by the small concentration of electrolytes necessary to produce the change, whereas a high concentration is necessary to salt out" (Hardy [illegible]).

By far the most interesting results, both practical and theoretical, are afforded by the classes of solutions sensitive to small concentrations of electrolytes.

1. *Coagulative powers of electrolytes.*—To a given volume of colloidal solution is added a quantity of electrolyte sufficient to produce coagulation (precipitation) of the disperse phase; if the molecular concentration of the electrolyte in the mixture be c, then $1/c$ is called the coagulating power of the given electrolyte on the given sample of the colloid. Among several samples of the same colloid one should express the coagulating powers of different electrolytes in terms of the necessary concentration per gram of the disperse phase per c.c. of sol.

Two remarkable results are evident on comparing the coagulative powers of various electrolytes on colloids of different kinds; first, the coagulation depends entirely on the ion bearing a charge of sign opposite to that of the colloidal particle and, second, with solutions of salts trivalent ions have, in general, immensely greater coagulative power than divalent ions, and the latter, in turn, much greater than univalent. Acids and alkalies in particular cases act more strongly than the corresponding salts.

Real systematic work on this phenomenon was first undertaken by Schulze,[9] and Linder and Picton,[10] and others [9] from a chemical point of view. The coagulative powers of different salt solutions were determined by the former for arsenious sulphide and antimony sulphide, and by Linder and Picton for arsenious sulphide; they found that this power depended solely on the valency of the metal ion. According to the latter workers, equivalent (equi-molecular) solutions containing monovalent, divalent, and trivalent metallic ions would possess, whatever the nature of the anion, coagulative powers in the ratios of 1 : 35 : 1023. As pointed out by Whetham [11] these numbers may be represented nearly by the formula $1 : x : x^2$. Such ratios have been confirmed by many other workers, both for negative and positive colloids, so that one is justified in referring to the formula as expressing the Schulze-Linder-Picton law.

In the bibliography at the close of this chapter may be found a list of some of the principal contributions to this phase of the subject. We may say that as a general rule the Schulze-Linder-Picton law has been found to hold, particularly for the salts of the light metals. Salts of heavy metals and many organic salts, which are absorbed in substances in anomalously large amounts, show a correspondingly anomalously large coagulating power.

Many writers have shown that, in any given case, a certain minimum quantity of electrolyte must be added to a given sample of colloidal solution before any coagulation can set in, and that there is always a time element involved in coagulation such that there may be no apparent change for some hours and then sudden coagulation of the whole solution.

A critical examination of the results of coagulation experiments will show that comparisons between the work of different persons must not be too rigid because the coagulating power of any given electrolyte varies greatly with the treatment of the sample used. As shown by the work of Spring,[12] Freundlich,[13] Hober and Gordon,[14] Paine,[15] Galecki,[16] and others, the question as to whether a given concentration of an electrolyte will produce coagulation or not depends, within a certain range, on how the electrolyte is added, e.g. slowly, drop by drop, or rapidly, with very gentle stirring or violent stirring, etc., and on how the mixture is treated immediately after the addition, e.g. whether shaken violently, heated and then cooled, heated for some time at the boiling point, etc. Naturally we may suppose that each experimenter carries out all his observations under similar conditions, and consequently that his results may be compared with one another, although the numbers determined by one worker may not agree entirely with those found by another.

Recent work by Mines [17] supports the view that emulsoids may ultimately be included under the same law as the suspensoids if the value of x in the formula $1 : x : x^2$ be taken very much larger than in the case of the latter.

2. *Electrokinetic effects of added electrolytes.*—Jevons first suggested that the coagulating action of electrolytes was due to the neutralization of a charge possessed by the particles. Hardy found that globulin solutions were most easily coagulated at the point where their charge was zero, i.e. at the time when they showed no motion in an electric field (the isoelectric point). Following Hardy's suggestion, experiments were carried out by the writer [18] to determine the influence of added electrolytes on the mobilities of the particles of gold, silver, and copper Bredig solutions.

Billiter,[19] in making similar experiments on colloidal solutions of platinum, mercury, silver, gold, and palladium, to which he added gradually increasing amounts of various electrolytes, found that the mobility of the particle gradually decreased and eventually changed its direction, showing that even the sign of the charge was changed by the addition of the electrolyte. He added gelatine and urea to his solutions in order to prevent coagulation. Whitney and Blake [20] disagree *in toto* with the conclusions of Billiter, and fail to reproduce his results with colloidal solutions of gold and platinum, free from gelatine. They assign Billiter's change in the direction of migration to the dissolved gelatine. In the following experiments the addition of traces of various salts to colloidal solutions of gold, silver, and copper (without the addition of a third substance such as gelatine or urea) brought about in each case a change in the direction of the migration of the particles in an electric field.

Since, in the case of gold and silver solutions, the particles are negatively charged, while in copper sol the particles are positively charged, the potent ion in the former solutions should be the metallic (positively charged) ion, whereas the ion coagulating the copper particle should be that from the acid radicle (i.e. negatively charged). The results of experiments on gold and silver will be given separately from those for copper.

The solutions used were prepared in pure water by Bredig's electrical method, and the mobilities were measured as already described (p. 131).

In each case (silver and gold solutions) the mobility was measured for the pure solution: varying quantities of aluminium sulphate were then added to fresh samples of the stock colloidal solution and the mobility again measured. Aluminium sulphate was used because the metal ions being trivalent have a large coagulative power; if these ions in producing coagulation do diminish the charge on the particles, a very small addition of aluminium ions should have a perceptible effect on the mobility of the particles, while at the same time the specific conductivity, and consequently the current through the colloid, is small.

·001N aluminium sulphate was added drop by drop to some 40 c.cs. of the colloidal solution, the whole well mixed and the mobility measured; each experiment was completed in the course of two hours after adding the electrolyte. In Tables XXII and XXIII the mobilities corresponding to the various weights of aluminium per 100 c.cs. of colloidal solution are given; a gradual decrease in the mobility and final reversal of direction is shown in each case. The positive sign in the mobility column indicates motion of the particles toward the cathode.

Samples of each of the solutions to which the electrolyte had been added were inclosed in test-tubes and the rapidity of coagulation observed. With the silver, solution no. 2 coagulated within a few hours, no. 3 had settled slightly after standing all night, while no. 4 took longer to coagulate than no. 3. With the gold, solutions nos. 2 and 3 both coagulated at the end of a few hours, while no. 4 had not completely coagulated after standing for four days. In each case the pure solution was stable indefinitely.

TABLE XXII.—SILVER SOLUTION.

Amount of silver per 100 c.cs. = 6·5 mgs.

No.	Grms. of Al. per 100 c.cs.	Spec. conductivity of solution at 18° C.	Mobility at 18° C.
1	0	$28{\cdot}5 \times 10^{-6}$	$-22{\cdot}4 \times 10$ [illegible]
2	14×10^{-6}	$29{\cdot}7 \times 10^{-6}$	$-7{\cdot}2 \times 10$ [illegible]
3	38×10^{-6}	$30{\cdot}3 \times 10^{-6}$	$+5{\cdot}9 \times 10$ [illegible]
4	77×10^{-6}	$31{\cdot}0 \times 10^{-6}$	$+13{\cdot}8 \times 10$ [illegible]

TABLE XXIII.—GOLD SOLUTION.

Amount of gold per 100 c.cs. = 6·2 mgs.

No.	Grms. of Al. per 100 c.cs.	Spec. conductivity of solution at 18° C.	Mobility at 18° C.
1	0	$3{\cdot}6 \times 10^{-6}$	-33×10 [illegible]
2	19×10^{-6}	$5{\cdot}2 \times 10^{-6}$	$-17{\cdot}1 \times 10$ [illegible]
3	38×10^{-6}	$6{\cdot}6 \times 10^{-6}$	$+1{\cdot}7 \times 10$ [illegible]
4	63×10^{-6}	$11{\cdot}6 \times 10^{-5}$	$+13{\cdot}5 \times 10$ [illegible]

These results point quite clearly to the existence of an isoelectric point for such solutions, for it is quite apparent that the particle passes through a state of maximum instability at the time when its charge is changing from negative to positive. Figure 16 illustrates the results recorded in Tables XXII and XXIII.

A very striking result of these experiments is the fact that, after passing through the isoelectric point, an increase in the quantity of electrolyte added produces an increase in the stability of the solution. When the minutest traces of aluminium sulphate are added to the colloidal solution, it appears that all of the aluminium ions go to decrease the charge on the particle, and when aluminium is added in quantities just sufficient to neutralize that charge, coagulation of the particles is most rapid. When, however, the electrolyte is added at once in excess of this quantity, the particles act as absorbers of the metallic ions, and the charge on the particle is thus changed at once from a large negative to a large positive one; this positive charge on the particle induces the same stabilizing effects as the negative charge, and so maintains the colloidal particles in the state of fine subdivision.

A more complete series of similar experiments were carried out on the copper colloidal solutions. They deal with, first, the effect of solutions of two salts having the same acid radical and, respectively, a monovalent and a trivalent metal, viz. potassium sulphate and aluminium sulphate, and, secondly, the effect of solutions of salts having the same metal ion and, respectively, monovalent, divalent, and trivalent, acid radicals, viz. potassium chloride, potassium sulphate, potassium phosphate, and potassium ferricyanide.

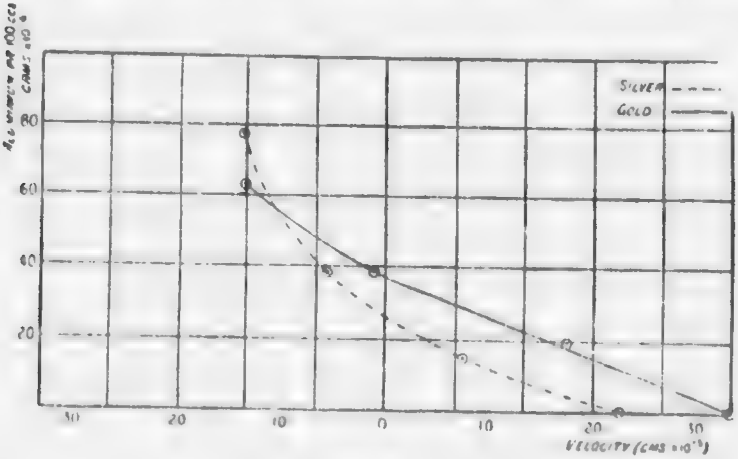

FIG. 16.

A typical series of experiments on the effect of each of the electrolytes was as follows: The mobility of the particles in the pure copper solution was first taken, gradually increasing quantities of the chosen electrolytic solution were then added to fresh samples of the stock copper solution and the corresponding mobility measured each time. The measurement of one mobility was usually completed within one hour of the addition of the electrolyte.

In order to illustrate the relation between the number of molecules of the various electrolytes added per c.c. of the copper colloidal solution and the resulting mobility of the copper particles, all of the results are brought together in Table XXIV and illustrated in the curves in Fig. 17. Column II gives the normality, in respect of the electrolyte, of the mixture of the colloid and the electrolyte, i.e. the number of gram-molecules of the salt per c.c. of the mixture. According to the accepted dissociation theory we may look upon the salts in these extremely dilute solutions as being completely ionized, and so the normality as defined above will be directly proportional to the number of ionized

TABLE XXIV.—RELATION BETWEEN THE NUMBER OF NEGATIVE IONS ADDED PER C.C. TO THE COPPER COLLOIDAL SOLUTIONS AND THE RESULTING MOBILITIES OF THE PARTICLES.

Solution.	Normality gram-mols. per c.c.	Numbers proportional to the number of ions per c.c.: Grm.-ions per c.c.	Mobility at 18° C.
KCl: 1	0	0	+ 24·9 × 10⁻⁵
2	17·0 × 10⁻⁶	17·0 × 10⁻⁶	+ 25·7 × 10⁻⁵
3	38·0 × 10⁻⁶	38·0 × 10⁻⁶	+ 26·2 × 10⁻⁵
4	74·0 × 10⁻⁶	74·0 × 10⁻⁶	+ 22·8 × 10⁻⁵
5	154·0 × 10⁻⁶	154·0 × 10⁻⁶	+ 18·7 × 10⁻⁵
K_2SO_4: 1	0	0	+ 25·4 × 10⁻⁵
2	7·7 × 10⁻⁶	7·7 × 10⁻⁶	+ 25·3 × 10⁻⁵
3	19·2 × 10⁻⁶	19·2 × 10⁻⁶	+ 24·0 × 10⁻⁵
4	38·4 × 10⁻⁶	38·4 × 10⁻⁶	+ 21·8 × 10⁻⁵
5	96·0 × 10⁻⁶	96·0 × 10⁻⁶	+ 14·4 × 10⁻⁵
6	153·0 × 10⁻⁶	153·0 × 10⁻⁶	0·0 × 10⁻⁵
$Al_2(SO_4)_3$: 1	0	0	+ 23·4 × 10⁻⁵
2	4·6 × 10⁻⁶	13·8 × 10⁻⁶	+ 21·5 × 10⁻⁵
3	9·2 × 10⁻⁶	27·6 × 10⁻⁶	+ 19·2 × 10⁻⁵
4	18·3 × 10⁻⁶	54·9 × 10⁻⁶	+ 18·5 × 10⁻⁵
K_3PO_4: 1	0	0	+ 25·4 × 10⁻⁵
2	3·6 × 10⁻⁶	3·6 × 10⁻⁶	+ 21·5 × 10⁻⁵
3	7·2 × 10⁻⁶	7·2 × 10⁻⁶	+ 16·8 × 10⁻⁵
4	14·4 × 10⁻⁶	14·4 × 10⁻⁶	+ 3·4 × 10⁻⁵
5	21·6 × 10⁻⁶	21·6 × 10⁻⁶	− 4·8 × 10⁻⁵
6	32·8 × 10⁻⁶	32·8 × 10⁻⁶	− 7·9 × 10⁻⁵
$K_6(FeCy_6)_4$: 1	0	0	+ 30·4 × 10⁻⁵
2	3·55 × 10⁻⁶	7·1 × 10⁻⁶	+ 14·0 × 10⁻⁵
3	7·15 × 10⁻⁶	14·3 × 10⁻⁶	+ 3·8 × 10⁻⁵
4	10·7 × 10⁻⁶	21·4 × 10⁻⁶	+ 1·0 × 10⁻⁵
5	14·3 × 10⁻⁶	28·6 × 10⁻⁶	− 1·5 × 10⁻⁵
6	21·4 × 10⁻⁶	42·8 × 10⁻⁶	− 9·1 × 10⁻⁵

molecules of the particular salt per c.c. However, if we are to compare the efficiency of various ions in discharging the colloidal particles, we must deduce numbers directly proportional to the number of such ions per cubic centimetre. For example, taking the above definition of normality, we may look upon a 3×10^{-6} normal solution of potassium phosphate as containing the same number of molecules as the number of molecules of potassium ferricyanide in a 3×10^{-6} normal solution of potassium ferricyanide. But the latter solution will contain twice the number of $FeCy_6$ ions that the former contains of PO_4 ions. Consequently in Column III are written the numbers directly proportional to the number of acid radical ions present per cubic centimetre; of course, those numbers opposite aluminium sulphate and potassium ferricyanide are the only ones which will differ in the two columns. In the last column are copied the various mobilities in cms. per sec. per volt per cm.

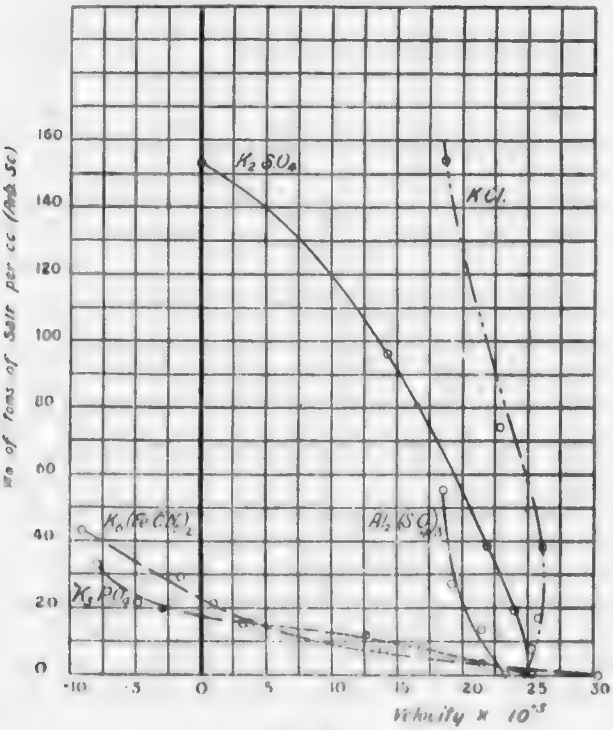

FIG. 17.

The curves in Fig. 17 are drawn with the mobilities as abscissæ and the numbers proportional to the number of ions per c.c. as ordinates. The very marked overlapping of the curves for potassium phosphate and potassium ferricyanide at once suggests the fact that the two ions PO_4 and $FeCy_6$ have the same power of reducing the mobility of the copper particle and, therefore, of producing the coagulation of the copper.

Although the experiments on aluminium sulphate were not carried out as far as those on potassium sulphate, nevertheless the corresponding curves show a remarkable coincidence in the region common to the two.

These latter two curves have an additional importance in that they show that the action of the SO_4 ion is practically independent of the metal ion. Since aluminium is trivalent and potassium monovalent, if the metal ions exerted any marked influence on the copper particle, we should expect these two curves to be very far apart.

Again, comparing the five curves, one has the very strongest evidence of the great differences in the powers of monovalent, divalent, and trivalent acid ions to reduce the mobility of the positively charged copper and, consequently, to produce coagulation. Examination of the curves will show that the mobility results indicate that the ratios of the powers of various acid ions to reduce the mobility of the copper particles are not very far removed from the observed ratios of the powers of the same ions to produce coagulation.

Hardy[8] suggested that coagulation by electrolytes takes place thus: the particles have their charges neutralized by the absorption of the oppositely charged ions of an electrolytic solution, and at the isoelectric point, where the charge becomes zero, the colloid coagulates. Following out this idea, Whetham[11] has given an explanation of the remarkable valency relations of the coagulative powers of electrolytic solutions. On the supposition "that in order to produce the aggregation of colloidal particles which constitutes coagulation, a certain minimum electrostatic charge has to be brought within reach of a colloidal group, and that such conjunctions must occur with a certain minimum frequency throughout the solution," he deduces that the coagulative powers of equivalent solutions containing monovalent, divalent, and trivalent ions respectively would be in the ratio of $1 : x : x^2$, where x is an arbitrary constant. If x is put equal to 32 this ratio reproduces, in a wonderfully exact way, the experimental numbers of Linder and Picton; the results, calculated and observed, are respectively 1 : 32 : 1024 and 1 : 35 : 1023.

Correlating Hardy's results with the Lippmann phenomenon regarding the connexion between surface tension and potential difference, Bredig [21] suggested a very plausible theory as to the precise causes bringing about coagulation. The surface tension of mercury in contact with an electrolytic solution reaches a maximum when the potential difference between the two phases is zero.[1] If we assume that the colloidal particles are kept in their state of fine subdivision in the liquid medium by the surface tension between the particle and liquid, then anything which tends to decrease the potential difference between the particle and the liquid will lessen the force opposing surface tension. Such lessening of the potential difference is brought about by the absorption by the particles of ions bearing a charge opposite in sign to that on the particle; now, as the surface tension effect is increased, the particles tend to decrease the surface exposed to the liquid by uniting with one another and thus bring about coagulation.

3. *Action of electrolytes in electroendosmose.*—The intimate connexion, already pointed out, between the motion of the colloidal particle in an electric field and the phenomenon of electroendosmose has led to the examination of the effect of electrolytic solutions containing ions of different valencies on the latter phenomenon. Extensive researches on this point have been carried out by Perrin [22] and Elissafof.[23]

Perrin measured the rate of flow of a given liquid through a porous diaphragm when a potential fall of about 10 volts per cm. was maintained across the diaphragm. The various diaphragms were made in the form of cylinders about 1·5 sq. cm. cross-section and from 10 to 12 cms. long by packing the material in a glass tube. The liquid was drawn by the current towards one or other of the electrodes, depending on the composition of the liquid, but independent of the insoluble material of which the diaphragm was made; the substances used for the porous diaphragm were the following: aluminium oxide, naphthalene, chromium chloride, silver chloride, barium sulphate, boric acid, sulphur, salol, carborundum, gelatine, cellulose, silex, zinc sulphide, calcium carbonate, powdered glass, barium carbonate, and manganese trioxide. He found that only ionizing liquids (those with a high dielectric constant) gave appreciable electro-osmosis, and that of these liquids a medium feebly acid gave a positive charge to the walls of the diaphragm (i.e. the liquid moved toward the positive electrode), while in a medium feebly alkaline the walls became negatively charged, the liquid positively charged. He tried the effect of adding various electrolytes to each liquid medium and found that the charge given to the walls was usually diminished and then reversed in sign. Particularly strong effects were shown by the strong acids and bases, and by solutions of salts with polyvalent ions.

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[1] See note, p. 188.

"The electric potential of any wall whatever in aqueous solution is always raised by the addition to the solution of a monovalent acid; it is always lowered by the addition of a monovalent base.

"Having given a liquid which gives to a wall an electrification of a certain sign, the addition to this liquid of a polyvalent ion of the opposite sign diminishes greatly the electrification of the wall and sometimes even reverses the sign, the electrification then obtained being, however, generally much below that given by the ions H^+ and OH^-. Further, the influence of divalent ions is generally very much less than the influence of trivalent ions, which are in turn much weaker than tetravalent ions."

The latter statement is a generalization from experiments on the diaphragms mentioned above with the following electrolytic solutions: lanthanum, barium, calcium, and cobalt nitrates, magnesium chloride, manganese sulphate, acid potassium carbonate, potassium ferro- and ferri-cyanides, acid potassium phosphate, oxalic and citric acids.

Although Perrin's results do not permit us to give definite numbers to show the ratios of the discharging powers of monovalent, divalent, trivalent, and tetravalent ions, they point to an action analogous to that in the coagulation of colloidal particles. In a manner exactly parallel to the latter phenomena, the positive ions in salt solutions do not seem to affect a positively charged wall, while a negatively charged wall is not affected by the negative ions in solution. Perrin develops this parallel action exhaustively in his article.

Recently Elissafof[23] examined similar effects of salts on the electro-osmosis shown in capillary tubes of glass and quartz, placed in strong electric fields. Pure water moves in a capillary tube to the negative electrode; the addition of electrolyte to the water lessens this motion and often reverses it. In this action the kations are the powerful agents, the effect varying rapidly with the valency of the kation but being independent of the valency of the anion. Inorganic salts of the light metals act according to a valency law, analogous to the Schulze-Linder-Picton law for the coagulation of colloids. In agreement with recent work by Freundlich and his co-workers on coagulation, Elissafof found that the kations of acids, heavy metal salts, and salts of light metals with organic basic ions gave abnormally large effects.

Quite recent work by McTaggart[24] on the charge possessed by bubbles of gases in liquid media gives similar results for the action of ions of different valencies. By varying the composition of the aqueous medium, air bubbles can be made to move either to the anode or the cathode. Bubbles possessing a given charge have their motion decreased and then reversed by adding small quantities of electrolytes; analogous valency phenomena are present in this case also. The ion bearing a charge opposite to that of the bubble is the potent discharging factor of the added salt, the action depends entirely on the valency of this ion, and is apparently quite independent of the valency of the other ion.

In view of the parallelism between these electroendosmose effects and the coagulative powers of various ions, there can be very little doubt that we are dealing with very closely related phenomena.

4. *Ultramicroscopic observation of electrolytic action.*—Recent direct observation with the ultramicroscope leaves no doubt that the addition of electrolytes to a colloidal solution causes the condensation of small particles into larger ones which easily settle. As we have already noted, early observers of the Brownian movement—Jevons, Gouy, Spring—found that cessation of this motion and consequent coagulation resulted from the addition of electrolytes to suspensoids. The ultramicroscope in the hands of Zsigmondy, Cotton and Mouton, Maltézos, and others, showed that, on the addition of the electrolyte, the particles in the sol increased in size.

Cotton and Mouton [25] describe thus the effect of adding small traces of aluminium sulphate to Bredig silver sols: "When one examines with the ultramicroscope the flakes constituting the coagulum, one distinguishes a large number of brilliant points crowded closely together, and the idea which suggests itself to the mind is that these flakes are formed of the colloidal particles themselves, which have been brought together to form a coherent mass. . . . If one allows a small quantity of aluminium sulphate to diffuse slowly into a sample of the sol (Bredig silver sol) in the ultramicroscope, one sees that the aspect of the sol is changed little by little. Instead of the isolated points of light absolutely independent, there will be seen groups, composed at first of only two or three points which are evidently bound together. If one waits some time, the number of such groups goes on increasing while at the same time larger groups resembling strings of beads come into evidence. . . . It should be emphasized that, at least in this case, the particles are not stuck together and do not touch one another. If they were touching, one should not be able to distinguish one from the other once coagulation has set in. Not only are they separated by microscopic distances, but they possess, at least at first, a certain independence. In the groups formed by a small number of grains, the Brownian motions which still persist are not identical for the different grains. It is undoubtedly this structure which leads to the spongy flakes of which the coagulum is usually composed."

A new phenomenon has been brought to light by the experiments of Mayer, Schaeffer, and Terroine,[26] who worked with sols of gold, silver, platinum, arsenious sulphide, and ferric hydroxide. They find that the addition of traces of alkali has the effect of increasing the size of [illegible] colloidal grains if the colloid is positive, and of decreasing the size if the colloid is negative. The addition of traces of acids produces the reverse effect. This suggests that the reason alkalies have a stabilizing effect on such sols as platinum is that the grade of dispersion is made higher by the alkali (see C. Henry,[27] and Chassevant and Posternak [28]).

The results of recent work on this point may be summarized as follows (Reissig,[29] Wiegner,[30] Galecki,[31] Oden and Ohlon [32]):—

(*a*) A very slight electrolytic content causes no apparent lessening in the number of the particles.

(*b*) In a sample of colloid to which small quantities of electrolyte have been added, the number of its sub-microns may increase slightly at the expense of its amicrons, although there may be no indication of colour change in the sample (e.g. gold sol).

(*c*) The electrolytic coagulation of colloids which contain particles of various sizes progresses by the condensation of small particles on those of a larger size and not by the coalescence of particles of equal size. The larger ultra-microns act as condensation nuclei for the smaller particles.

(*d*) The colour changes of sols (e.g. gold) which accompany the addition of electrolytes run parallel to ultramicroscopic changes, in that the size of the particles increases and their number decreases as more and more electrolyte is added.

5. *Changes in physical properties due to electrolytes.*—Apart from the microscopic observation of the individual particles and the motion of those particles in an electric field, the physical properties by which the coagulative action of salts has been most often traced are (1) the colour, (2) the viscosity of the solution.

(1) *Colour changes.*—These changes indicate that there is a gradual increase in the size of the individual particles in the solution in the early stages of coagulation. Distinct varia-

tions in the colour of samples of gold and silver solutions have been observed by many workers. In the case of gold sols, as first surmised by Faraday,[2] and later proved by Zsigmondy,[33] Gutbier and Resenscheck,[34] by the addition of coagulating reagents the colour goes through the following series of changes: red, purple-red, red-violet, blue-violet, and deep blue, the Tyndall phenomenon becomes more and more evident, the solution becomes turbid, and finally the disperse phase separates in the form of powder, flakes, or gels. Carey Lea,[35] and Von Meyer and Lottermoser[36] have traced similar changes for silver solutions from dark brown, through brownish red and brownish violet, and then to a deep green.[37] As a usual thing other solutions become simply muddy or cloudy without any distinct colour change.

(2) *Viscosity changes during coagulation.*—As noted by Freundlich,[38] although we know very little of the theory of the viscosity changes produced in a medium by dissolving substances which give even molecular disperse (true) solutions, still "as long as we use viscosity for comparative experiments alone—for comparing different qualities and different sols—it is of the greatest value. . . . We can detect (easily) very slight changes in solutions by measuring viscosity."

In the main, three different methods of measuring the viscosity of colloids have been used: (1) velocity of flow through capillary tubes (e.g. Ostwald viscosimeter), (2) logarithmic decrement of an oscillating disk, (3) torque on concentric cylinders (e.g. Couette's apparatus[39]). These three methods do not in general give rigidly concordant results on account of the variations in the distribution of the shears in the liquid layers (see Garrett,[40] Hardy[41]). Various writers have pointed out the many complexities present in colloidal solutions which will affect the value of the viscosity: the prominence of different elements affecting the viscosity will depend on which of the above methods is used for the determination. These various contributing circumstances may be enumerated as follows: the internal friction of each of the several phases, the surface friction of the internal surfaces, the surface tension of the internal surfaces, the density of the electrical charge at the internal surfaces, the shape of the particles, the nature of the surface of the particle as to the absorption layer, and probably the degree of dispersion.

Einstein[42] first developed a theoretical formula for the viscosity (η_1) of a suspension of rigid spheres in any liquid, terms of the viscosity (η) of the pure liquid and the ratio (of the volume of the matter suspended to the volume of the medium, viz. :—

$$\eta_1 = \eta(1 + k . f),$$

where k is a constant. The value of the constant k has been calculated by many workers to be from 1·0 to 4·75 (see Einstein,[42] Hatschek[43]) and experimentally tested by others (Bancelin,[44] Harrison,[45] Freundlich and Ishasaka [46]) for suspensions of rather large particles. The values for k found experimentally vary over a large range even for the larger particles, while, in the case of small particles in suspension (Oden,[47] Woudstra[48], the linear law expressed in the above equation is departed from. However, a rigid experimental test is almost out of the question, first on account of the fact that the formula is developed for the case of smooth spheres in suspension, and secondly from the necessity of obtaining exactly the volume of the disperse phase, not merely the weight.

In any case, the above formula will apply only to solutions containing particles which are not deformable, and which amount to considerably less than 50 per cent of the total volume of the system. Hatschek[39] has deduced a completely different formula for the variation in the viscosity of the emulsoids.

However, entirely apart from theoretical considerations as to the laws governing the changes, such alterations in the viscosity will always indicate some corresponding change in the sols. Woudstra[48] has tried the effect of adding electrolytes to solutions of silver, ferric hydroxide, and chromium hydroxide; he found an ultimate slight increase in the viscosity due to additions of electrolytes even in quantities insufficient to cause any measurable variation in the viscosity of pure water when added to it. There is in his work the suggestion of the stronger action of the ions of higher valencies. Freundlich and Ishasaka[46] have made unique use of viscosity changes in measuring the rate of coagulation of aluminium hydroxide sols, and here again the valency of the active ion is important.

Although there has been an immense amount of work done on the viscosity changes of such sols as blood and rubber solutions, no very settled conclusions have as yet been arrived at. The whole question of the interrelation of viscosity, mobilities of ions and particles, and electrical conductivity, bristles with unsolved difficulties (see Hardy,[41] McBain,[49] Ostwald[50] and Pauli[51]).

6. *Ions entrained by the coagulum.*—When the phenomena of coagulation was first studied from a chemical point of view, analysis of the coagulum (precipitate showed that the latter always * absorbed, during the process of coagulation, a portion of the electrolyte instrumental in producing the change. Crum,[3] as early as 1854, found that in the coagulation of suspended aluminium hydroxide, the coagulum always contained small quantities of the acid or salt necessary for the coagulation. In their exhaustive study of colloidal solutions, as represented by metallic sulphides, Linder and Picton[10] found, in the case of the coagulation of arsenious sulphide particles (- ve), by the addition of barium chloride, that the coagulum carried down a distinct amount of the metal (+ ve ion) but none of the acid radicle. That this portion entrained was intimately bound up with the coagulum was demonstrated by the fact that by digesting the coagulum noted above with other metallic solutions, e.g. ammonium chloride, the entrained metal ions barium) could be replaced entirely in the course of a few days by other metals, e.g. ammonium. This same work was confirmed and extended by Whitney and Ober,[52] who showed, in addition, that the amounts of the metals calcium, barium, strontium, and potassium entrained by the coagulum from the same amount of a given colloid were exactly proportional to the equivalent weights of these metals (electrochemical equivalents). Whit-

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* Van Bemmelen suggests the use of *adsorption* for the surface phenomenon and *absorption* for the volume phenomenon. We shall use *absorption* alone as it is practically impossible to keep the two phenomena distinct.

ney and Ober were able to assign to the coagulum the formula $Ba . 90 (As_2S_3)$, which tends to substantiate the claim that we are here dealing with complex chemical combinations.

Spring[53] studied the action of electrolytes by observing the diffusion of the electrolytes from a strong solution, e.g. copper sulphate, into a supernatant layer of the suspensoid, e.g. mastic sol; the layer of copper sulphate at the surface of contact was robbed of its copper while the liquid at this level showed the presence of sulphuric acid. Similar results were also found with various metallic chlorides; Spring ascribes this phenomenon to hydrolysis of the salts in solution and absorption of the metal ions by the colloidal particles.

Duclaux's[54] explanation of the absorption of the ions of the precipitating electrolyte is that the latter are merely substituted for other ions—his so-called active part of the colloidal unit already entangled in the colloidal particle while it is still in the state of suspension. For instance, in the production of colloidal copper ferrocyanide by the interaction of potassium ferrocyanide and copper chloride, the colloidal particle retains proportions of the potassium varying between the limits indicated by the formulæ $(FeCy_6)Cu_{1·30}K_{1·28}$ and $(FeCy_6)Cu_{1·94}K_{0·12}$, which may also be written thus

$$(FeCy_6)\,Cu_2 + \tfrac{1}{2}\,(FeCy_6)\,K_4 \text{ and } (FeCy_6)\,Cu_2 + 1/30\,(FeCy_6)\,K_4.$$

In the case of the coagulation of this negative colloid by the metal ion, e.g. hydrogen, barium, aluminium, etc., "instead of the so-called entrainment by coagulation, the action will consist in the substitution of the hydrogen, etc., ions for a corresponding number of potassium ions." In the light of his results, Duclaux regards the colloidal particle as a product of purely chemical reaction.

On the other hand, the similarities between the absorption phenomena of colloidal solutions and the absorption effects of various solids, e.g. charcoal, lead one to suspect the existence of some specific absorptive power possessed by the surface of solids. This relationship has been developed by the following series of experiments:—

1. The absorption of liquids, colloids, and gases by insoluble powders as carried out by Thoulet,[55] Schmidt,[56] Davis,[57] McBain,[58] Van Bemmelen,[59] Nils Carli,[60] and others.

2. The absorption of electrolytes by the gels of coagulated colloids, as carried out first by Crum[61] and Warrington,[61] and recently by Van Bemmelen and his pupils,[59] Godlewski,[62] and others.

3. Recent work by Freundlich and his co-workers on the absorption by the colloidal particles during the process of coagulation.

Van Bemmelen differentiates between the phenomenon exhibited by porous bodies, charcoal, powdered glass, etc.—a distinctly surface effect which he calls adsorption—and the more intimate union producing a homogeneous solution of one substance in another—a distinctly volume effect which he calls absorption. As far as the experiments on the ions entrained either by the dried gels of sols when shaken in solutions of salts, or by the particles during coagulation, there is a probability that both adsorption and absorption intervene—a circumstance which would add to the complexity of the problem.

The recent work by Freundlich and his co-workers pushes further the researches of Linder and Picton, Spring, Whitney and Ober, and Duclaux. As a connecting link between this work and that of Van Bemmelen we may quote the experiments of Frion[63] on the action of barium sulphate precipitate in entraining magnesium and lanthanum ions during precipitation from solutions in which those ions are present. He found that the amount of these ions carried down by the barium sulphate precipitate depended on the acidity or basicity of the solution, the concentration of the entrained ion in the solution, and the valency of the entrained ion. The lanthanum ions (trivalent) were absorbed ten times as strongly as the magnesium ions (divalent).

The significant fact added to our knowledge by the work of Whitney and Ober[64] was that the ions of electrolytic solutions were absorbed by a given quantity of a certain colloid in amount exactly proportional to the electrochemical equivalent weights of these ions; i.e. the amounts of calcium, strontium, barium and potassium respectively were roughly proportional to ½(40), ½(87·7), ½(137·4) and 39·1. Freundlich and Schucht[64] have shown that the same law holds for other colloids—a fact which points to coagulation taking place when a certain charge of the opposite sign is brought up to the colloidal particle. Further, according to Freundlich ("Kap. Chem.," p. 354), for a given colloid, ions of differing valency are absorbed equally strongly in equimolecular concentrations of the ions in solution. Consequently, if in order to produce coagulation of a given colloid, a number of ions sufficient to supply a given charge must be brought up to each particle, solutions of monovalent, divalent, and trivalent ions necessary and sufficient to produce coagulation will have to be in decreasing order of strength. In addition the strengths necessary must be determined by a consideration of the absorption of the colloidal particles for ions of electrolytes.

Freundlich adopted the variation of Henry's law,[65] which expresses the absorption of various solids, to express the absorption process of colloids and tested the result experimentally. We shall present it here in its simplest form. If the molecular condition of the solute in the solvents is the same, Henry's law for the distribution of a body between two imniscible solvents is

$$C_a = \beta \,.\, C$$

where C_a and C_b are the concentrations of the body in the two solvents *a* and *b*, and β is a constant. If, however, the molecular weight of the solute in the solvent *b* is *n* times that in the solvent *a*, the equation takes the form

$$C_a = \beta \,.\, C_b^{\frac{1}{n}}.$$

Adapting this equation to the absorption by colloids Freundlich writes it:

$$v = a \,.\, C^{\frac{1}{n}},$$

where v = amount of given substance absorbed by unit mass of the colloid,

C = concentration of the absorbed substance in the sol, and a, n = constants for a given colloid.

Various workers have applied this formula to the absorption by charcoal and other solids of various electrolytes and dye solutions: the values of 1/*n* (Freundlich, "Kap. Chem.," pp. 150-1) lie between 0·11 and 0·50. Freundlich has proved the truth of the formula for various colloids (e.g. Freundlich and Schucht, with mercury sulphide). He finds 1/*n* to lie between 0·14 and 0·20 for the various colloids studied. Paine[15] found for Bredig colloidal copper, 1/*n* to be 0·16.

Putting in the values of 1/*n* such as those recorded, we have the resulting curve of the form illustrated in Fig. 18, from which we see that, for very small concentrations, the percentage of salt absorbed is very large, whereas for increasing concentrations, the curve becomes asymptotic to a line parallel to the axis of concentrations. If this curve represents the absorption by a given colloid of all electrolytes, irrespective of the valency of the ions, then at small concentrations of monovalent, divalent, and trivalent absorbable ions, the number of ions absorbed by the colloid may be such that, for the monovalent type, there is absolutely no coagulative action, whereas for the divalent or trivalent type, there may be sufficient to cause more or less rapid coagulation. For example, "Freundlich found that for a hydrosol of arsenious sulphide containing 1·80 grams per litre, 0·003 milligram-molecules of aluminium

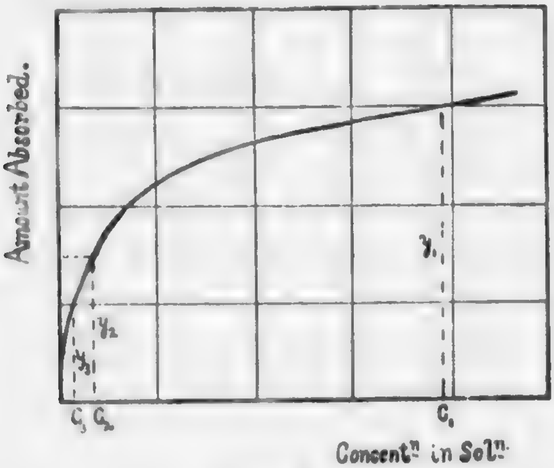

FIG. 18.

nitrate (or the equivalent of cerium sulphate) were required per litre for coagulation. The amount of the ions absorbed per gram of arsenious sulphide is given as about 0·087 milliequivalents, or 0·162 milliequivalents for one litre of the above solution, i.e. 0·054 milligram-molecules in the case of a trivalent ion. This would mean that about 50 or 60 per cent of the trivalent ions (present in the electrolyte necessary for coagulation) was absorbed by the colloid in its coagulation, as compared with a small fraction of 1 per cent (of the amount necessary for coagulation) of the monovalent ions."

If, in addition, as the work of Whitney and Ober, Freundlich, and others seems to indicate, electrochemically equivalent quantities of various ions must be absorbed in order to produce coagulation, we see from the absorption curves that the concentrations of ions of different valencies necessary to produce coagulation may easily differ in accordance with the Linder-Picton-Schulze law. If y_1 represents the number of monovalent ions necessary to produce coagulation in a given sample of colloid, that quantity will be absorbed from the electrolytic solution in which these ions have a concentration C_1; the quantity of divalent or trivalent ions necessary for the same coagulative result will be given respectively by $y_2 = 1/2\ y_1$ and $y_3 = 1/3\ y_1$, which correspond to the absorption from solutions of concentrations C_2 and C_3, respectively. A simple inspection of the absorption curve will show that there exists a wide range of values to the ratios $C_1 : C_2 : C_3$.

Freundlich has found exceptional agreement with this theoretical result in the case of salts of the light metals, while the salts of heavy metals and those with complex organic radicles seem to be absorbed in abnormally large quantities by colloids. Freundlich's conclusion is that "it follows necessarily that the coagulative power of a given salt depends greatly both on the valency and on the absorption coefficient, because with different (ionic) values, either of valency or absorption, very different concentrations are necessary in the solution in order that the equivalent quantity of the (active) ion shall be absorbed".

II. COAGULATION BY MIXING POSITIVE AND NEGATIVE COLLOIDS.

Linder and Picton [10] were the first to point out the classification of colloids into the two classes, cationic and anionic, according as the particles migrated in an electric field to the negative or to the positive electrode. They also were the first to note that, under certain conditions, a colloid bearing a charge of one sign added to one bearing a charge of the opposite sign brings about precipitation of the two colloids—a phenomenon confirmed by Lottermoser.[37]

This phase of the behaviour of colloids has been very completely investigated more recently by Niesser and Friedemann [65] and Biltz.[66] The latter has shown that, as in the case of coagulation by electrolytes, the immediate precipitating action depends greatly on the manner in which the two colloids are mixed, i.e. whether slowly drop by drop, or rapidly with shaking. For colloids mixed together quickly and treated uniformly, Biltz enunciated the following laws:—

(1) If to a given colloid one of opposite sign be added in small proportion, there is no precipitating action.

(2) As the quantities of the second colloid added at once are increased the coagulative action becomes more and more noticeable, until a proportion is reached which causes immediate coagulation.

(3) As this amount is still further increased coagulation ceases to appear; that is, there is an optimum of precipitating action shown for certain proportions, and if in any case these favourable proportions are exceeded on either side, no precipitating action takes place at all.

(4) With the exception of a sol of selenium, which may have some anomalous chemical action, mixing two sols of the same sign produces no precipitation at any stage.

Billiter [67] showed that, when two colloids of opposite sign were mixed, with one in excess, the direction of migration of the whole was always the same as that of the colloid in excess.

The whole of this mutual coagulative action points undoubtedly to the electrical nature of coagulation. It is believed that the particles in excess in a mixture of two oppositely charged colloids are attracted and absorbed by the other particles to such an extent that there results a larger unit, the charge of which is the same in sign as that of the absorbed particles. At the time of maximum precipitating action, the numbers of each kind of particle are just sufficient to produce uncharged masses which coalesce by surface tension and fall to the bottom.

One would conclude from such action that the proportion of the two colloids in the precipitate would approximate to a constant quantity, which is in accordance with experimental results; in fact, many reactions formerly believed to be purely chemical are really of the above nature as, for example, tannin and gelatine, tannin and basic colours, basic and acid colours, etc.

In general, the charges on the particles of emulsoids are much less apparent than in the case of suspensoids and the phenomena resulting from mixing emulsoids are of much greater complexity. Allied to this is the action of various colloids and salts on suspensions of bacteria, which has been investigated particularly by Niesser and Friedemann,[68] Bechhold,[69] and Buxton and his co-workers.[70]

III. Protective Action of certain Colloidal Solutions (Schutzkolloide).

Many organic colloids (emulsoids) when added, in comparatively minute quantities, to suspensoids have the power of preventing the coagulation of the suspensoid particles. The consensus of opinion seems to be that, on account of the surface tension relations between the medium, the suspensoid particle, and the emulsoid substance, the latter surrounds the suspensoid particle with a thin coating which prevents the coalescence of the particles, either by preventing the cause which brings about coagulation (the discharge of the particles), or merely by offering a material obstacle to the coalescence.

Many examples of this protective action have been furnished by various workers. Quantitative determinations of the protective action of organic colloids have been worked out thoroughly by Zsigmondy[71] and others in relation to gold sols and by Müller and Artmann[72] in relation to arsenious, antimony, and cadmium sulphides. The results for gold solutions are expressed by what Zsigmondy has called the gold-value of the given organic colloid. This gold-value is defined as follows: "The gold-value of a given protecting colloid (Schutzkolloid) is the number of milligrams of the colloid required to protect 10 ccs. of a stable gold solution, containing from 0·0053 to 0·0058 per cent of gold, from the precipitating action of 1 cc. of a 10 per cent solution of sodium chloride". Gelatine has much the lowest gold-value, the substances in an ascending series of gold-values being gelatine, casein, egg-albumen, and gum arabic, all of which have strong protective action. Dextrin and various kinds of soluble starch also act as protectors but to a lesser extent than the above named substances.

Since the discovery of the protective action of these substances it has been found that many so-called colloidal solutions owe their very existence as colloids to the presence of some protecting substance in small concentration. Reference to the classification in Table III (*Ie*) and Table IV (Class 5) will show to what a great extent this phenomenon plays a part.

Undoubtedly the action of protective colloids is of first importance in many practical applications of colloidal study. The fluids of the body, so extensively colloidal in their nature, may alter greatly in their action as their content of protecting colloids varies. Again, in agriculture, the humus of the soil is probably a protecting colloid and as such will have a far-reaching effect in retaining the richness of the surface layers.

IV. ACTION OF VARIOUS RADIATIONS ON SOLS.

The intimate connexion between coagulation and the charge possessed by the particles is shown by the action of β rays of radium on typical solutions. The γ rays, which are probably of the nature of X-rays, have been found to have no effect on the sols; the α (positively charged) rays of radium have not sufficient penetrating power to affect the particles in any considerable volume of the solution. The β rays have sufficient penetrating power to traverse a layer of a solution some centimetres thick, and, as they possess a negative charge, they should exert a discharging effect on any positively charged particles and thereby hasten coagulation, while any effect on negatively charged particles should be that of increasing the charges and thus stabilizing the solution.

Hardy[73] tried the effect of β rays on sols of purified globulin dissolved in (*a*) acetic acid, and (*b*) sodium hydroxide; as already noted the globulin particles in solution (*a*) are cationic, i.e. positively charged, while those in (*b*) are anionic, i.e. negatively charged. The effect of the β rays was to bring sample (*a*) to the state of a jelly in three minutes, whereas the particles in solution (*b*) were rendered more mobile in an electric field, i.e. showed an increase in charge.

Henri and Mayer[74] found that exposing a sample of a sol to radium bromide had no effect in the cases of the pure sols of silver and ferric hydroxide, but that when a electrolyte, e.g. sodium nitrate, was added to the sols in quantity much too small to produce coagulation, the silver sample remained uncoagulated while the ferric hydroxide was coagulated, when both were again exposed to the β rays from radium. A sample of hæmoglobin was coagulated by the β rays in seven hours.

Dreyer and Hanssen[75] exposed samples of albumen to the influence of ultraviolet light and found that coagulation set in. Careful experiments carried on under the writer's direction on the influence of strong ultraviolet light on a sol of copper in methyl alcohol (positively charged particles) gave no coagulation of the particles.

Spring[12] tried the discharging effect of X-rays and that of the brush discharge from a Holtz machine and of the discharge of an induction coil on samples of mastic, silica, Bredig solutions of gold, silver, and platinum, but obtained a negative result in every case. Later[76] he tested the transparency of such sols for X-rays but found no abnormal absorption by the solutions.

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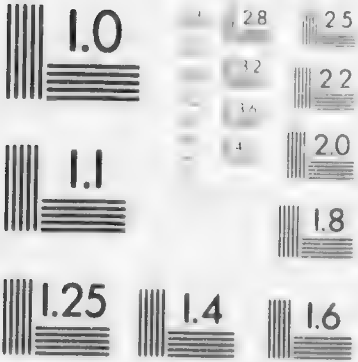
MICROCOPY RESOLUTION TEST CHART

ANSI and ISO TEST CHART No. 2



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CHAPTER IX.

THEORY OF THE STABILITY OF COLLOIDS.

SEVERAL attempts have been made to give a general theory of the colloidal state, applicable to all classes of sols. The problems of special interest, from a theoretical point of view, may be classified into three main divisions :—

1. What is the process by which the disperse phase is produced in the solution?

2. What are the forces which assure the stability of such a state?

3. What is the nature of the coagulation of sols by the addition of electrolytes, or, in a few instances, of non-electrolytes?

Naturally these questions must ultimately be treated as a whole, but in each of the theories which have been proposed stress has been laid particularly on one or other of these points. In what follows, these questions will be considered chiefly in relation to dispersoids, but the bearing of the phenomena on emulsoids will also be noted briefly.

I. THE PRODUCTION OF THE DISPERSE PHASE.

It has already been shown that the methods of preparation of dispersoids fall naturally into two classes: (*a*) condensation methods, in which the particles grow from molecular sizes to the colloidal size, and (*b*) dispersion methods, whereby large complexes of the colloidal material are broken up into the small colloidal particles. This subdivision suggests that the stable colloidal particle is, in every instance, an equilibrium state between two opposing sets of forces: viz. those tending to bring about the coalescence of small particles to form larger ones and those tending to cause the dispersion of the colloidal substance throughout the medium.

After the work of Linder and Picton,[1] Lobry de Bruyn,[2] Zsigmondy and Siedentopf,[3] and Svedberg[4] on the transition from coarse suspensions to ordinary molecular solutions, there can be little doubt that colloidal solutions do exist which contain particles of any size from that visible in the microscope to that of molecules. This view has induced workers to search after the laws which regulate the various forces at work in fixing, under any given conditions, the size of the particles.

Donnan[5] has offered a suggestion as to these laws. He assumes that the colloidal substance disintegrates in the liquid medium up to a certain grade of dispersion because the cohesive forces between the liquid and the solid are greater than the adhesive forces between the molecules of the solid. When the particles become so small that the liquid layer about them becomes thinner than the range of molecular attraction of the liquid, the forces of attraction due to the liquid will decrease and when they are just equivalent to the mutual attraction of the particles of the solid, the size remains constant. When the colloidal particles are produced by a condensation method, they will grow to the same limiting size fixed by the same limiting conditions. However, such a simple explanation of the phenomena will hardly account for the existence of colloidal solutions of such a wide range of concentrations and dispersity as we find between the extreme limits of Linder and Picton's arsenious sulphide solutions or Zsigmondy's gold sols.

Garnett[6] probably first states, in this regard, the bearing of the process of crystallization on the production of colloidal solutions. "When a homogeneous liquid separates into two states, say, a liquid and crystals, the new state (phase) appears first as minute droplets which represent an unstable state and which changes to the stable crystalline state in a longer or shorter time, according to the relative magnitude of the force of crystallization and the force due to surface tension. Substances which do not readily crystallize, whose molecules therefore have feeble polarity, permit the unstable emulsion state to become subpermanent, and this is the state known as colloidal solution."[7]

Von Weimarn[8] has developed similar ideas to account for all colloidal solutions. The two sets of forces are presented thus: "In agreement with the present view of crystallographers, a crystal presents a completely uniform system of points about which the molecules execute their harmonic motion; this is the so-called space-lattice. It is not hard to imagine that a free crystal surface in contact with the surrounding liquid medium, in which the crystal forms, must disturb, to a certain extent, the uniformity of these points and the motion of the molecules at this surface of separation. The layer at the crystal surface will approach in its properties the internal layers of a highly compressed liquid, just as at the surface of a liquid the transition layer will resemble in its properties the internal layers of a highly compressed gas. It would be a great mistake to assume that the conditions at the crystal-liquid surface of separation are the same as in an ordinary liquid. They approach one another but are not the same.

"Two factors play an important rôle in the production and properties of the free surface of the crystal, viz.:—

"A. the influence of vectorial molecular forces on the molecules constituting the free crystal surface, and

"B. molecular kinetic processes coming into play at the free crystal surface.

"The factor A gives rise to the capillary pressure which is added to the external pressure on the crystal face and which is magnified as the grade of the dispersion increases (i.e. as the size of the crystals decrease). Therefore, in general, this factor A causes the dispersed body to depart from the liquid state (i.e. increases the size of the particles), and this tendency is the stronger the greater the grade of the dispersion of the crystallizing body because, for most substances, the melting point is raised by an increase of pressure. Only in a few cases, e.g. ice, the factor A causes the dispersed substance to approach the liquid state, for the melting points of such substances as ice are lowered by increase of pressure.

"The factor B tends to cause all bodies, without exception, to approach the liquid state, because it lessens the regularity of the orientation of the molecules at the surface layers. Thus we see that in only a few cases will the factors A and B exert influences in the same sense. For the great majority of substances these two influences are diametrically opposed. Experiment shows us that the factor B works more energetically than A, because disperse crystalline bodies are more soluble, more fusible, more transitory, and have stronger reacting power, the higher the grade of dispersion—an effect which increases more and more as the liquid state is reached.

"It is not hard to confirm that the factors A and B struggle with one another for mastery, although the factor B comes out victor. The factor A acts more and more energetically the greater the surface tension, while the factor B, on the other hand, increases with the increase of the activity of the dispersion medium in relation to the disperse phase. . . . In this way we see that the physico-chemical properties are functions of the grade of the dispersion."

Following out this line of thought, Von Weimarn shows that the production of a colloidal solution in any given case will depend on the relative potency of these two factors under the given conditions of the reaction. He maintains that any substance whatever can be produced in the colloidal state provided the proper conditions of solubility, concentration, etc., are discovered. In confirmation of this thesis, Von Weimarn has produced over two hundred substances[9] in the colloidal state, many of them, e.g. ice, not having been previously so produced. Furthermore, he maintains that the initial stage in the evolution of any colloidal solution is the formation of small crystals; a statement which he holds to be true even for gelatine and agar-agar.[10] A corollary of this proposition is that there is no amorphous state of a substance in the sense of it being entirely non-crystalline; for example, a so-called amorphous powder or a gel is merely an aggregation of small crystals held together in small masses by the effects of surface tension (see Frankenheim[11]).

More particularly, according to Von Weimarn, in any so-called chemical reaction, when the rate of precipitation is low, there is produced a distinctly crystalline deposit; when this rate is high, one gets a higher degree of dispersion—a sol, a flocculent precipitate, or a jelly as the case may be; when two very concentrated solutions of substances which by their interaction produce a very insoluble precipitate, are mixed, a jelly always results. Even the most definitely so-called crystalloidal bodies may be obtained in the colloidal or gelatinized states if produced in solutions in which they are very insoluble. An ordinary precipitate such as barium sulphate is at first formed by the combination of the ions in very minute crystal elements which are sufficiently soluble in water rapidly to unite to form crystals, which gradually increase in size by absorbing the smaller crystal elements. It is well known in ordinary analytical work that such precipitates will pass at first through any filter, but gradually become filterable by the effects of time and warmth. If, however, their insolubility is sufficiently increased by large excess of a common ion, or by effecting the combination in a medium, such as methyl alcohol, in which the sulphates are extremely insoluble, the molecules cannot coalesce in the form of large crystals but remain in spherical masses and a colloidal sol results.[12] In this way some years ago, Paal[13] obtained in colloidal form the chlorides of sodium and potassium by the double decomposition of their organic compounds in organic media in which the chlorides were sufficiently insoluble.

In the cases of the dispersion methods of preparation, Von Weimarn treats the electrically prepared metal sols as, in reality, the result of the condensation of small crystals from the vapours of the metals, and the colloids produced by re-solution of a precipitate, e.g. peptization, merely as samples of changes in the solubility of the precipitate due to the stabilizing ion.

The theory put forward by Von Weimarn dispenses with the view suggested by Schulze,[14] Carey Lea,[15] and others that in colloidal solutions we have allotropic forms of the various substances involved; the allotropy is merely in the massing of the individual minute crystals.

In addition to the forces outlined by the above theory, we must take account of the effect of the charge on the particles, especially in the case of most suspensoids. In view of the work of Hardy on the globulins alone, one cannot neglect the effect of the electrical charges at any stage of the process. It may be that Von Weimarn includes them tacitly in the forces under factor A; nevertheless, in the equilibrium state of the colloid, the charge on the particles is important enough to demand special attention.

The problem of accounting for the charge possessed by colloidal particles has led to the suggestion of various theories as to the production of the colloidal particle. There can be no doubt that this charge is due primarily to some chemical combination followed by a partial dissociation of a portion of the colloidal unit. It is quite possible that these chemical actions may vary greatly in the nature and still bring about similar final results. Two or three examples of this may suffice.

Duclaux[16] and Jordis[17] have shown pretty conclusively that, with such colloids as ferric hydrate, copper ferrocyanide, etc., produced by double decomposition, the particles constituting the disperse phase consist in the main of the chemical compound named, but that this compound always retains a certain amount of one of the primary reacting substances, which in some way gives the charge to the particle. Conversely, Duclaux accounts for peptization by saying that this process adds to the precipitate to be redispersed the ions which produce the charge on the particles. In line with Duclaux's suggestion is Hardy's discovery that the charge possessed by globulin particles depended on whether the medium was acidic or basic. As another instance of some chemical action, the writer[18] (p. 142) has given evidence to show that the charge possessed by the metallic particles of the Bredig electrically prepared solutions is due to a chemical reaction between the medium and the metal followed by dissociation.

II. THE CAUSE OF THE STABILITY OF COLLOIDAL SOLUTIONS.

Practically every one who has attempted to account for the stability of colloidal solutions assumes that they are two-phase systems. The distinctions raised are as to the relations of the two phases: (1) the purely physical theory looks upon the sols merely as suspensions of fine particles, each one of which is self-contained; (2) Quincke's theory assumes that the system of particles in the liquid medium constitutes a foam-like structure, the surrounding liquid being a true solution of a very slight amount of the disperse phase in the pure solvent, while the walls of the structure are solutions of a small quantity of the liquid in the solid. The latter is practically the view of Van Bemmelen as given by the adsorption compounds. In any case, the forces which determine the stability of the sol, i.e. which keep the disperse phase from precipitating in response to gravity, are in the main: (1) surface tension, (2) electrical repulsions, and (3) the Brownian movements; to these Duclaux has added the force due to osmotic pressure.[19]

Up to the present, attempts to account for the stability of both suspensoids and emulsoids by the same theory have been so unsuccessful that we are driven to divide them, as suggested by Woudstra[20]: "When we picture to ourselves the sols as structures of two phases with very great areas of contact, there are two possibilities: the surface of contact of the two phases is continuous or it is not. In the first case we might imagine the sol as a honeycomb scaffolding of water dissolved in the colloid, surrounded by an aqueous solution of the colloidal material. In the second case, the sol consists of a number of discrete particles of the colloid which, under certain influences, are able to defy gravity and remain divided in the water which forms the medium. . . . To the first group belong gelatine, albumen, egg-albumen, silicic acid, etc., i.e. emulsoids in general; to the second group (suspensoids), metal sols, sulphide sols, hydroxide sols, etc." As has already been pointed out, these two groups differ in two particulars which have an exceedingly important bearing on their stability. First, those of the emulsoid group move little, if any, in an electric field, i.e. the particles show little if any charge and, secondly, probably as a result of this lack of charge, these colloids are much less sensitive to added electrolytes than are the suspensoids. Following Quincke, then, we may assume that the all-important factor in the stability of emulsoids is the surface tension between the two continuous phases of the sol.

On the other hand, we have in the case of the suspensoids, in addition to surface tension, the electrical forces due to the charge. The potential energy due to surface tension, T, possessed by an area, A, is T × A, and, since the coalescence of particles will reduce the total surface area, in order to have the surface energy due to this cause a minimum, small particles will tend to coalesce into larger ones. At the same time, if each particle bears a definite charge, the coalescence of such particles will bring about an increase in the potential energy due to the charge. Equilibrium will result when these two effects just counterbalance. That is, the total potential energy of the particles will be the sum of all such quantities as :—

$$T \times A + \tfrac{1}{2} E \,.\, V, \; [\text{or } T \times A + \tfrac{1}{2} E^2/C, \text{ or } T \times A + \tfrac{1}{2} CV^2]$$

where T represents the surface tension between the particle and the liquid, V, the potential difference between the particle and the liquid, and A, C, and E respectively the area, capacity, and the charge of each particle. In the case of spherical, conducting particles bearing charges of a certain definite size and surrounded by an outer layer of ions of an opposite charge, the capacity of a single particle will be (p. 130)

$$C = K \,.\, r^2/d,$$

where r is the radius of the solid core of the particle,
d is the average distance between the surface of the core and the outer layer,
and K is the dielectric constant of the medium.

The coalescence of two such particles reduces the capacity of the two and therefore increases the potential energy due to the charges on the particles.

We may say then that the charges on the separate particles keep them separated while the forces of surface tension, if left to themselves, would cause coalescence and consequent coagulation. As seen from the three forms of the equation for the potential energy above, anything which lessens the value of

V when C is unchanged, will decrease the potential energy and consequently weaken the force opposed to surface tension. When possible this will take place and consequently the sol will tend to coagulate when V is decreased.

So far there is fair agreement in the views of various workers; a great deal of discussion has taken place on the question as to how the particles really become charged. On account of the similarities between colloidal and electroendosmose experiments, the early workers accounted for the mobility of the particles in an electric field by saying that there is a contact difference of potential between the particle and the liquid. In view of our lack of knowledge of what contact difference of potential really means, such a statement is hardly an explanation of how the charging comes about. Particles were known to become either positively or negatively charged, and examination of various results led Coehn [21] to formulate the following empirical law: "A substance of higher dielectric constant charges itself positively when it comes in contact with a substance of smaller dielectric constant". Later Heydweiler [22] showed that this law did not hold in the cases of metals and liquids.

Since the work of Perrin,[23] there is no doubt that the process is due to electrolytic ions. Early workers (e.g. Bredig [24]) adopted the principle enunciated by Nernst,[25] viz. that every ion possessed a specific solution pressure in any given liquid, and conceived the complete colloidal unit to consist of a solid core charged by the loss of certain positive or negative ions which form an outer layer about this core: this is the double layer proposed by Quincke [26] and Helmholtz.[27] The principal differences expressed in the views of later writers have been merely regarding the nature of this dissociation. Billiter [28] suggested that the colloidal particle, e.g. silver, dissolves in accordance with Nernst's law, but only in the form of positive ions; consequently the core left is negatively charged. Thus an electrical double layer is formed on the surface of the colloidal particle, the outer layer positive, the inner layer negative. The writer, on the other hand, has submitted evidence to show that the dissociation in the cases of the

Bredig metal sols is really that of a layer of hydroxide or hydride on the surface of the metal particles (p. 138). Duclaux[1] believes that the charge always arises from the dissociation of a portion of extraneous substance retained by the particles from the reacting media; for example, he has shown that in the colloidal particles of ferric hydroxide, there is always retained a small trace of ferric chloride, which was used in the production of the sol. He pictures the colloidal particle thus: an inner solid core of ferric oxide, surrounded by a layer of ferric chloride; this latter layer dissociates, in the Nernst manner, leaving an excess of positive iron ions on the solid core and, as an outer layer, an atmosphere of negative chloride ions.

As a conclusion, in the present state of our knowledge of these solutions we may make the statement that the existence of the colloidal particle is fundamentally due to an equilibrium maintained between the forces of surface tension and the repulsion due to the electrical charges. In a stable colloid, settling to the bottom of the vessel in obedience to gravity is prevented, in the case of sufficiently small particles, by the molecular shocks which give rise to the Brownian movement.

III. THE NATURE OF THE COAGULATION OF SUSPENSOIDS.

In any view that is taken of the process involved in coagulation the following experimental results have to be kept in mind:—

1. In coagulation by added electrolytes, only the ion which bears a charge of sign opposite to that on the colloidal particle is involved. For example, the discharging action of the various negative ions on copper colloidal particles (Bredig sols) seems to be entirely independent of the valency of the positive ions with which they are associated (p. 153 *et seq.*).

2. A portion of the electrolyte producing the coagulation is always carried down by the coagulum.

3. As a general rule, the coagulating power of ions depends solely on their valency; except in odd cases showing anomalous absorption effect, the Linder-Picton-Schulze law holds fairly well.

4. Whether a given amount of salt solution will coagulate a given sample of colloid or not depends on the rate at which the salt is added and the subsequent treatment as to heating, shaking, etc.

5. Coagulation is a process requiring time; after the addition of the electrolyte, there is an initial period during which no appreciable effect takes place. This initial period may vary from a few seconds to days.

6. According to Paine[29] the relation between the rate of coagulation and the concentration of the colloid shows that the coagulative process follows the law of mass action, and indicates that coagulation is brought about directly by the mutual attraction of the particles.

From these experimental data we see that the dominating factor in bringing about coagulation of the dispersoids is undoubtedly the neutralization of the charge possessed by the particle. This may conceivably be done by so altering the properties of the liquid medium itself that the dissociation producing the electric double layer is lessened; this would bring about at least a partial recombination of the two charged layers. However, in most cases the experimental results point to an absorption by the particle of ions bearing a charge opposite to that of the particle.

Billiter[28] supposed that the mobility of a colloidal particle in an electric field was due to the fact that, under the influence of the electric field, ions diffuse off the outside of the double layer into the surrounding medium and leave the colloidal unit with a net charge similar to that on the core itself. This colloidal particle then moves similarly to an ion. Billiter's further assumption that this net charge is much below the charge on an ion and that coagulation represents a condensation of these particles about an ion, does not seem to be in agreement with the general experimental results. Nevertheless, we may consider, after Billiter, that any outer layer is a constantly changing system of ions; when a foreign electrolyte is added, there is an increase in the concentration of ions about the particle and, on account of some absorption effect, which may be due to surface concentration or merely strong electrical attraction, a certain number of ions of charge opposite to that on the core are drawn on to the core itself and thus produce the discharging effect. Freundlich at one time suggested that the surfaces of colloidal particles act as semipermeable membranes with respect to ions, and that, in the case of a negatively charged particle, the migration velocity of positive ions is accelerated on passing the outer layer, while the velocity of negative ions is reduced; and conversely for positively charged particles.

The influence on coagulation of shaking the mixture, quick addition of the electrolyte, etc., and the existence of the initial, apparently quiescent period during coagulation, lends colour to the view, as expressed in Whetham's theory,[30] that the discharge of the particles and consequent coalescence, depends on a charge of a certain size being brought up to the particle.

It is sometimes objected that such a theory cannot be applied to explain peptization. However, there is no reason why the converse effect may not take place when the stabilizing ions are added to the moist coagulum to be peptized. An analogous phenomenon has been recorded by the writer: exceedingly small doses of aluminium sulphate added to a Bredig silver sol produces coagulation; if to a series of similar samples of the sol increasingly large amounts of the sulphate are added, it is found that the coagulative power of the salt goes through a maximum, and that large doses produce a fairly stable sol, in which, however, the particles are found to have changed from negatively charged to positively charged, presumably from the adsorbed aluminium ions.

Granted that the particles are necessarily discharged before coagulation sets in, the question as to how the coalescence occurs still remains. Three active agencies are at work before the discharge has taken place, viz. surface tension, Brownian movement, and electrical repulsions. The first will always tend to cause decrease in the total surface by coalescence, the Brownian movement will continually tend to bring the particles into collision, but the electrical forces will always tend to prevent the particles approaching one another very closely. Anyone who has watched the movement of the particles either in liquids or gases will be struck by the fact that collisions do not appear to take place; two or three particles may approach one another, rotate about a common centre for a few moments, and then break away. One is driven to the conclusion that they are held apart by considerable forces, while they are always knocked helter-skelter by the molecular shocks. Once the electrical repulsion is materially reduced, the surface tension forces come into play to cause coalescence.*

Two unique views of coagulation have recently been brought forward (1) by Duclaux,[19] and (2) by Tolman.[32] Following out his experiments on the osmotic pressure exerted by the colloidal particles relatively to the dispersion medium, the former suggests that the coagulating solutions added to the colloid produce throughout the colloid regions of negative osmotic pressure, which regions act as starting points for coagulation. Tolman, treating the colloid system as a special case of general dispersoid systems, comes to the conclusion that, for equilibrium in any colloidal solution, all the particles must be of the same size; in order to have permanent stability in a dispersoid, he finds that the surface tension must be zero. Equality of size in any given sample of any colloid hardly agrees with the observations of Zsigmondy and others on the sizes of particles.

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* One often observes in papers that the effects of surface tension and of electrical charge are confused; it is often said loosely that the electrical charge lessens the surface tension. As shown by many experiments,[31] an electrical charge does not affect the surface tension *per se*. Moreover, the dimensions of the mechanical tension on the surface of a charged body, due to the charge, are quite different from those of surface tension. Of course, in general, an electric charge will act so as to oppose the effect of the surface tension.

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CHAPTER X.

PRACTICAL APPLICATIONS OF THE STUDY OF COLLOIDAL SOLUTIONS.

THE practical applications of colloidal solutions are so widespread that entire volumes might be devoted to such questions as their relation to manufacturing processes, their occurrence and economic value in nature, and their importance in the physiology of the human body. We shall have to content ourselves with merely suggesting the outlines of this phase of the subject.

Processes essentially colloidal in their nature have been employed for many years prior to the development of the theoretical interest in colloidal solutions as such. Instances of this may be found in the manufacture of soaps, rubber, and paper, and in such processes as the extraction of sugar from beet-root.[1] Probably in no field has the theoretical treatment of colloidal solutions received wider application than in dyeing and the related industry of tanning.

Modern accounts of the process of dyeing take into consideration the colloidal state for two reasons: (1) the textile fibres to be dyed are colloidal in their nature, and (2) many of the dye solutions are true colloidal solutions. Michaelis,[2] Freundlich and Neumann,[3] and Biltz and Pfenning[4] have separated the dyes into three classes with regard to their colloidal nature: viz. (1) those in which nearly all the substance exists as visible ultramicrons and which may easily be subjected to dialysis, (2) those in which the substance exists as a mixture of submicrons, amicrons, and possibly molecules and which may be dialysed but only at a very slow rate, and (3) those which contain no visible ultramicrons but which show fluorescence and diffuse readily through parchment paper.

The action of the dyes of these various classes is determined by the extent of their colloidal properties. Many writers have given a colloidal theory of the whole process of dyeing; the relation of the electrical charge possessed by the particle of the dye to the action has been particularly emphasized by Gee and Harrison,[5] and by Feilmann,[6] while the function of mordants as a phase of colloidal behaviour is suggested by Krafft[7] and others. Wood[8] unifies the various conflicting theories of the process of dyeing by pointing out that this process is really dual in its nature, the two stages in the process being (1) absorption of the dye by the fibre tissue, and (2) the fixation of the dye in the fibre. The first stage is, in general, an example of the absorption phenomena of colloids as detailed by Van Bemmelen, whereas the fixation may be purely chemical in some cases or, in others, merely a precipitation of a colloid by salts.

The evolution of the photographic plate[9] serves as a striking example of the use of gelatine and similar colloids in arts and industries. In the everyday operations involved in baking, distilling, and dairying, colloidal solutions are always occurring, and many of the reactions are regulated by the laws of these solutions.

It is probable that no one substance is of more interest from its colloidal nature than common clay. In the manufactures of cement and porcelain, in the purification of effluent waters, and in the treatment of various soils, the colloidal properties of clay are of the first importance.

Clay is defined as the mineral part of the soil and consists mainly of rock material divided into particles less than 0·002 mm. in diameter (Russel[10]); pure clay consists of "complex silicates containing much iron and alumina," while clay as it is used in the manufactures and as it exists in fertile soils will be mixed with varying proportions of calcium carbonate and phosphate, organic matter, soil water containing carbon dioxide in solution, and residues of plants.

The setting of cement is now thought to be due to the slow coagulation of the hydroxides of silicon, aluminium, and iron and the action of the absorbed carbon dioxide in forming after a time hardened calcium carbonate. The admixture of gravel to form concrete provides nuclei about which the coagulation takes place. The plasticity of the clay, so important in porcelain manufacture, is explained by the fact that the clay in the air-dried state contains substances which dissolve in water in the colloidal state. In common with many other colloids, clay in suspension has great absorptive power, not only for various ions in solution but also for many other substances both in the crystalloidal and colloidal states. In the coagulation of clay solutions, the coagulum will carry down the various absorbed substances. Since clays absorb and retain substances such as "oils, fats, concentrated soap solutions, starch dextrine, maltose, glycerine, plant and animal albumin, casein, inorganic dyes such as Prussian blue and Turnbull's blue, all coal-tar dyes . . ., animal colouring matters such as carmine, the colouring matter of the blood, the yellowish-brown colouring matter of urine, fæcal matter, further, all bad odours, certain hydrocarbons, and kinds of ions—they are suitable for clearing, decolourizing, and purifying the effluent waters of factories and works, which contain substances in the colloidal state, and many colouring matters, those of the carbohydrate industries, starch and dextrine, dyeing, tanning, soap-boiling, paper and sugar works, breweries and distilleries, and finally town sewage".[11] Such a coagulation is of daily occurrence in the formation of deltas at river mouths; on meeting the salt water of the ocean the silt of the river water is coagulated quickly.

The greatest economic importance of clay is as an essential element of a good agricultural soil; its importance is not so much on account of its chemical composition as it is due to the colloidal nature of the clay. "It is a mistake to suppose that the medium on which the soil organisms live and which is in contact with the plant roots, is the inert mineral matter that forms the bulk of the soil. Instead the medium is the colloidal complex of organic and inorganic compounds, usually more or less saturated with water, that envelops the mineral particles; it is therefore analogous to the plate of nutrient jelly, used by bacteriologists, while the mineral particles serve mainly to support the medium and control the supply of air and water and, to some extent, the temperature."[12] The great absorptive power of these surface colloids in the soil suffices to retain near the surface practically the whole of any food added to the soil; this results in time in the development of a rich humus at the surface. Whatever the view taken of the necessary composition of the soil colloids,[13] there is unanimity in ascribing to the colloids the essential actions of a good soil: for example, the formation of compound fine particles in the humus, the absorption of soluble manures, the retention of water, the ascent of water from great depths (Linde[14]), the swelling of the soils when wet and the contraction when dry, are probably all essentially colloidal phenomena.

The extensive interest developed recently in colloidal solutions has had important bearing on the study of physiology. Advances have been marked in two directions: (1) the increased power of observation afforded by the ultramicroscope, and (2) the extended study of the body fluids as colloids. Under the first heading, we may draw attention to the new bacteria first identified by the use of the ultramicroscope, such as those relating to yellow fever, foot and mouth disease, certain forms of cholera, and tobacco disease; again, Raehlmann's ultramicroscopic study[15] of blood and urine has confirmed our knowledge of these fluids under various conditions, e.g. he identified particles of albumen in the urine of nephritic patients. In the second place, studies of such problems as the change in the viscosity of the body fluids under changing circumstances,[15] the influence of salts on the properties and action of the blood,[17] and the laws regulating the permeability of cell walls for salts and colloids in the human body, are bound to advance both our knowledge of the action of the normal body and our power of treatment of abnormal conditions.

In all these phases of the practical applications of the work on colloidal solutions we see what a vast unexplored region is still before us.

In spite of the immense amount of work that has been done during the last fifteen years, it is quite apparent that, both from a theoretical and a practical point of view, there still is need for much additional research before one would be able to suggest, with any degree of satisfaction, a general theory of the colloidal state. We may very well conclude with the words used by the pioneer worker Zsigmondy,[18] in closing his first account of the early work on colloidal solutions :—

"From the foregoing outline no general theory of colloids can be given, for the study of colloids has become a great and extensive science, in the development of which many must assist; only when the voluminous material supplied by much physico-chemical research has been properly systematized, will the theory of colloidal solutions be raised from mere consideration of the similarities in special cases to the standing of an exact science."

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